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THE Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

WHINFIELD,
SALCOMBE,
S. DEVON.
Sept. 18*th*, 1914.

GENTLEMEN,

I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1915, which is submitted for publication in the Society's Transactions and Proceedings, as hitherto. Some delay has occurred in presenting it owing to the disturbance of the postal arrangements on the Continent in consequence of the war, and to the illness of Professor Urbain.

The Report deals with all the determinations of atomic weights which have been published since the issue of the preceding Report; but, in accordance with the resolution of the Eighth International Congress of Applied Chemistry, no change in the official table of atomic weights will be made until after the meeting of the next Congress. It is recommended, therefore, that the table accompanying the Report for 1913 should be reprinted without alteration.

I have appended the signatures of Professors Ostwald and Urbain as desired by them, subject to a qualification by the latter

which he proposes to introduce in the French translation of the Report in connexion with the atomic weights of Ytterbium and Lutecium.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
London.

Annual Report of the International Committee on Atomic Weights, 1915.

The Council of the International Association of Chemical Societies, with which the Committee on Atomic Weights is now affiliated, recommended, at its meeting in September, 1913, that the annual report of said committee should be published in August. The present report, therefore, is submitted in compliance with that recommendation, although delays due to the difficulties of correspondence may sometimes prevent simultaneous publication in all countries.

Since the report for 1914 was prepared, a number of new atomic-weight determinations have been published. These may be briefly summarised as follows:

Silver, Sulphur and Chlorine.—Scheuer (*Arch. Sci. phys. nat.*, 1913, [iv], **36**, 381) dissolved pure silver in sulphuric acid, and collected and weighed the sulphur dioxide given off. The weighed sulphate was then converted into chloride by heating in a current of gaseous hydrochloric acid. Three ratios were thus determined, which gave the three desired atomic weights, independent of all former determinations. The results obtained are Ag = 107·884, S = 32·067, Cl = 35·460. The value for silver is rather high; the other values agree with those generally accepted.

Calcium.—Œchsner de Coninck (*Bull. Acad. roy. Belg.*, 1913, 222) has determined the atomic weight of calcium by conversion of the carbonate into the sulphate. His final value is Ca = 40·13.

Barium.—Also redetermined by Œchsner de Coninck (*Rev. gén. chim. pure appl.*, 1913, **16**, 245). Barium carbonate was dissolved in nitric acid, and the carbon dioxide so evolved was weighed. The value found was Ba = 137·36.

Copper.—Atomic weight determined by Œchsner de Coninck and Ducelliez (*Rev. gén. chim. pure appl.*, 1913, **16**, 122). Copper was oxidised by nitric acid, and the oxide was weighed. In five experiments they found Cu = 63·523 to 63·605; in mean, 63·549.

These atomic-weight determinations by Œchsner de Coninck are published in the briefest possible way, without any of the details that are commonly regarded as essential. How were the substances purified? Were the weights reduced to a vacuum?

Cadmium.—Quinn and Hulett (*J. Physical Chem.*, 1913, **17**, 780) have redetermined the atomic weight of cadmium by electrolysis of the chloride and bromide. In each series the cadmium was collected and weighed in mercury. From the chloride, with Cl = 35·458, Cd = 112·32. From the bromide, with Br = 79·92, Cd = 112·26. These values agree well with those previously found by Perdue and Hulett, and by Laird and Hulett, but are much lower than the value (Baxter's) adopted in the table. The cause of the difference is yet to be satisfactorily explained, but it must be due to a constant error in one or the other of the methods employed. A change in the table would be premature.

Mercury.—Taylor and Hulett (*J. Physical Chem.*, 1913, **17**, 755) prepared mercuric oxide by heating pure mercury in oxygen. Weighed amounts of the oxide were then decomposed by heating it with metallic iron, and the mercury was collected and weighed. From the data thus obtained, Hg = 200·37. This, as in the case of cadmium, is lower than the recognised value, and its acceptance or rejection must await further evidence.

Vanadium.—Atomic weight redetermined by Briscoe and Little (P., 1914, **30**, 64; T., 1914, **105**, 1310) from analyses of the oxychloride, $VOCl_3$. The mean value found was V = 50·950 but 50·96 is preferred.

Selenium.—Jannek and Meyer (*Zeitsch. anorg. Chem.*, 1913, **83**, 51) determined the atomic weight of selenium by oxidising Se to SeO_2. The mean of ten experiments gave Se = 79·140.

The same constant was deduced by Bruylants and Bytebier (*Bull. Acad. roy. Belg.*, 1912, 856) from the density of selenium hydride, SeH_2. In four series of experiments, the weight of a litre of the gas at 0° and 760 mm. was found to be 3·6715 grams. For the weight of a litre of oxygen under the same conditions they found 1·4295 grams.* By the method of limiting densities, and with H = 1·008, Se = 79·18, which is near the value given in the table.

Tellurium.—Dennis and Anderson (*J. Amer. Chem. Soc.*, 1914, **36**, 882) purified tellurium by preparing the hydride, TeH_2, from aluminium telluride, and condensing the gas to solid at the temperature of liquid air. From the hydride the metal was obtained by heating to 500°. Thirty-one conversions of Te thus

* According to Germann (*Compt. rend.*, 1913, **157**, 326), the normal litre of oxygen weighs 1·42900 grams.

prepared into TeO_2 gave in mean Te=127·6. Other determinations by a volumetric method gave a lower value, near 127·50. The authors conclude that the higher, hypothetical "dvitellurium" does not exist.

Scandium.—Lukens (*J. Amer. Chem. Soc.*, 1913, **35**, 1470) prepared scandium oxide from Colorado wolfram. By calcination of the sulphate to oxide he found Sc=44·59 and 44·77. The material was probably not quite pure.

Yttrium.—Meyer and Weinheber (*Ber.*, 1913, **46**, 2672), by conversion of yttrium oxide into sulphate, found Yt=88·75. By the reverse process they found Yt=88·74. Corrected to a vacuum, this becomes 88·70.

Ytterbium and Lutecium.—Atomic weights reinvestigated by Auer von Welsbach (*Monatsh.*, 1913, **34**, 1713). For ytterbium (aldebaranium) he found Yb=173·00. For lutecium (cassiopeium), Lu=175·00.

Iridium.—Holzmann (*Sitzungsber. phys.-med. Soz. Erlangen*, **44**, 84) made four reductions of the salt $(NH_4)_2IrCl_6$ in hydrogen, and found Ir=193·42. This is higher than the accepted value, and not conclusive enough to justify a change.

Helium.—Heuse (*Ber. Deut. physikal. Ges.*, 1913, **15**, 578), in seven determinations of the density of helium, finds the weight of a normal litre to be 0·17856 gram. Hence, by the method of limiting densities, He=4·002.

Neon.—From two determinations of the density of neon, Leduc (*Compt. rend.*, 1914, **158**, 864) finds Ne=20.

No changes of serious importance seem to be needed in the atomic-weight table. Possibly the values for yttrium, ytterbium, helium, and neon should be changed, but such action may well be deferred until next year. Some experiments by Richards and Cox (*J. Amer. Chem. Soc.*, 1914, **36**, 819) on the purity of lithium perchlorate also suggest a possible lowering in the atomic weight of silver, namely, from 107·88 to 107·871.

(*Signed*) F. W. Clarke.
W. Ostwald.
T. E. Thorpe.
G. Urbain.

Note.—Since this report was finished and approved, Professor Urbain has informed us that, jointly with M. Blumenfeld, he has re-determined the atomic weight of neoytterbium with great care. The earth was subjected to many fractionations, and each fraction was studied magnetically and spectroscopically. The value found for the atomic, the mean of thirteen determinations, was 173·50.

1915.

International Atomic Weights.

		0=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6

		0=16.
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

He suspects that the "aldebaranium" studied by Auer von Welsbach contained an element of lower atomic weight, probably thulium. Urbain's paper will be published in the near future, perhaps before this report appears. F. W. C.
T. E. T.

The following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions*:

197. "Interaction of alkali alkyl sulphates and alkali nitrites: theories of the formation of aliphatic nitro-compounds." By Panchānon Neogi. (Trans., 1914, 2371.)

Aliphatic nitrites and nitro-compounds have been prepared by the interaction of the alkali salts of methyl-, propyl-, *iso*butyl-, and *iso*amyl-sulphuric acids and sodium, potassium, calcium, and barium nitrites. The theory of tautomerism is discussed, and two new theories, namely, those of "isomeric conversion" and "additive combination," are advanced.

198. "The influence of acids and alkalis on the optical activity of some amino-acids." By John Kerfoot Wood. (Trans., 1914, 1988.)

The author has determined the optical activity of leucine, aspartic acid, and glutamic acid in aqueous solution and in the presence of varying amounts of hydrochloric acid and of sodium hydroxide. It is shown how it is possible to calculate from the results of the experiments the degree of hydrolysis of the salts of the amino-acids and the basic and acidic ionisation-constants of the latter. The values obtained for the basic ionisation-constants of leucine and aspartic acid are in very close agreement with those arrived at by other methods.

199. "The velocities of flame in mixtures of methane and air." By Albert Parker and Alan Victor Rhead. (Trans., 1914, 2150.)

The velocities of the flame of mixtures of methane and air in different proportions have been determined at different points in 2·5 cm. tubes of glass, copper, iron, and lead. Thin strips of Wood's alloy (melting at 72°) stretched across the tubes at various points were used as flame indicators. The metal bridges were placed in electrical connexion with a magnet, which operated a stylus on a revolving drum. It has been found that the propaga-

tion of flame in mixtures of methane and air occurs in three distinct periods when fired from an open to a closed end of a tube. In the first period the flame travels with a constant and uniform velocity. The second period consists of vibratory movements and a sudden increase in velocity. In the third period the rate again falls to a uniform value as the flame approaches the closed end.

In tubes of the same diameter the initial velocity of explosion varies with the material of the tube; the velocity is less in tubes possessing a higher conductivity for heat.

The most explosive mixture, which contains 10 per cent. of methane, possesses an initial velocity of 70 cm. per second. The velocity decreases with change of the amount of methane present, moving towards zero at 4·5 and 13·1 per cent. The effect of a bend in the explosion tube has been found to vary with the percentage composition of the mixture.

200. "Experiments on the migration of para-halogen atoms in phenols." By Ivan Richard Gibbs and Philip Wilfred Robertson. (Trans., 1914, 1685.)

The authors have studied the action of nitric acid on certain *p*-bromo-*m*-cresols in which one of the ortho-positions is free. In only one instance was the migration of bromine observed, namely, in the case of 4 : 6-dibromo-*m*-cresol, which yielded on nitration the 2-bromo-4 : 6-dinitro-derivative:

201. "Some derivatives of safrole." By Robinson Percy Foulds and Robert Robinson. (Trans., 1914, 1963.)

6-*Nitrosafrole* was prepared, and found to be readily reduced to 6-*aminosafrole*, the *acetyl* derivative of which could be changed to either a quinoline or an indole derivative. 6-Nitrosafrole, on oxidation with permanganate, yielded 6-*nitropiperonylacetic acid*, which could not be further oxidised to a nitropiperonylic acid.

202. "Position-isomerism and optical activity." By Julius Berend Cohen. (Trans., 1914, 1892.)

The paper contains a critical examination of the theory of Frankland and Wharton (T., 1896, **69**, 1583), by which they

attempt to explain the numerical relation subsisting between the rotatory power of position-isomerides when attached to an active side-chain. The author shows from the large amount of data collected by himself and his collaborators on the substituted menthyl esters of benzoic acid that the theory cannot be sustained.

203. "Studies in catalysis. Part I. Hydrolysis of methyl acetate, with a theory of homogeneous catalysis." By Alfred Lamble and William Cudmore McCullagh Lewis. (Trans., 1914, 2330.)

Measurements of the rate of hydrolysis of methyl acetate in the presence of hydrion as catalyst have been carried out at 25° and 35°, and it is shown that the temperature-coefficient of the reaction is independent of the amount of the catalyst, a result which stands in opposition to the Arrhenius theory of "active" and "passive" molecules. A general theory of homogeneous catalysis is suggested, based on the magnitude of the infra-red radiation effects from hydrion, and it is shown that the quantity of energy required per molecule of methyl acetate to cause it to react is of the same order of magnitude as one quantum of infra-red radiation in the region of 5μ. Certain deductions from the theory are pointed out.

204. "The action of magnesium phenyl bromide on derivatives of phenyl styryl ketone." By Ida Smedley MacLean and Sibyl Taite Widdows. (Trans., 1914, 2169.)

The product of the interaction of magnesium phenyl bromide and phenyl *p*-carbethoxystyryl ketone is p-*carbethoxy-ββ-diphenylpropiophenone*. The corresponding *acid* was obtained in colourless needles melting at 184—185°; the *semicarbazide* melted at 220—221°.

Phenyl *p*-dimethylaminostyryl ketone, when similarly treated with magnesium phenyl bromide, gives *diphenyl-p-dimethylaminostyrylcarbinol*, $NMe_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CPh_2 \cdot OH$, melting at 100°.

205. "The firing of gases by adiabatic compression. Part I Photographic analysis of the flame." By Harold Baily Dixon, Lawrence Bradshaw, and Colin Campbell. (Trans., 1914, 2027.)

These experiments were undertaken in order to study the initiation of the flame produced by the adiabatic compression of gases.

The gases, contained in a stout glass tube, were compressed by a piston moving between supports and forced in by a falling pendulum; the flames produced were photographed on a rapidly moving film.

The photographs showed:

(1) That the piston was not stopped at the moment the gases reached their ignition-point, but at the moment the moving force was removed.

(2) That the nature of the flame depended partly on the rate at which the piston was driven in.

(3) That no violent compression waves were set up, although such waves did exist when the mixtures were fired by a spark.

(4) That explosive mixtures of gases did not "detonate" when they were fired by adiabatic compression, and that the real ignition-point was not synchronous with the appearance of the flame.

(5) That the pre-flame period is not negligible, and therefore in any determination of the ignition-temperature by this method the piston must be stopped at the beginning of the pre-flame period.

Some of the difficulties in using the method of adiabatic compression to determine the ignition-temperatures are discussed, and a number of preliminary results with mixtures of hydrogen and oxygen are given.

206. "The firing of gases by adiabatic compression. Part II. The ignition-points of mixtures containing electrolytic gas." By Harold Baily Dixon and James Murray Crofts. (Trans., 1914. 2036.)

An apparatus is described by means of which gaseous mixtures may be fired by adiabatic compression according to the suggestion of Nernst (see Falk, *J. Amer. Chem. Soc.*, 1906, **28**, 1517; 1907, **29**, 1536). The ignition-points were calculated from the formula $\frac{T_2}{T_1}=\left(\frac{V_1}{V}\right)^{\gamma-1}$, V_1, V_2, and T_1 being determined experimentally. For convenience, the value of γ, the ratio of the specific heat at constant pressure to that at constant volume, was taken as 1·4, all the gases used being diatomic. The main sources of error are discussed, and the effects of the lubricant, of changes in initial temperature and pressure of the gaseous mixture, and of the addition of other gases, are investigated.

The ignition-point of electrolytic gas is found to be 526°. The addition of excess of oxygen lowers the ignition-point until the limits of inflammability are reached; this is contrary to the results of Falk, who found that the mixture H_2+O_2 had the lowest ignition-point, and that the addition of more oxygen resulted in a raising of the ignition-point.

Nitrogen or hydrogen added to electrolytic gas raises the ignition-point progressively, and acts apparently as an inert gas. In the

case of the former, the ignition-point may be calculated with close approximation from the formula $t°_N=(526+11x)°$, where x is the number of volumes of nitrogen added to three volumes of electrolytic gas, the mixture being denoted by $2H_2+O_2+xN_2$. Similarly, for hydrogen mixtures, $2H_2+O_2+xH_2$, the ignition-point is given by the formula $t°_H=(526+18x)°$. The limit of inflammability is reached roughly by the mixture containing 14 volumes of added gas to 3 of electrolytic gas.

Attention is drawn to the peculiar effect of the addition of oxygen and to the fact that V_1 and T_1 remaining the same, V_2 for mixtures containing excess of hydrogen is less than the value of V_2 found for corresponding mixtures containing excess of nitrogen, and hence the calculated value for T_2 in the case of the former is greater than T_2 in the case of the latter.

207. "The chemical constitution of dioximines."
By Leo Alexandrovitsch Tschugaev. (Trans., 1914, 2187.)

In 1905 the author discovered a new series of complex compounds of the heavy metals corresponding with the eighth group of the periodic system and derived from $\alpha\beta$-dioximes, for example, $Ni(D_2H_2)$, $Pt(D_2H_2)$, $[Co{\cdot}2NH_3{\cdot}D_2H_2]Cl$, etc.,

$$\left[D_2H_2 = \begin{pmatrix} R{\cdot}C{:}NOH \\ R{\cdot}C{:}NO \end{pmatrix}_2\right].$$

The structure of these compounds, termed by the author dioximines, is discussed, and experimental evidence in favour of the general formula of the group $M(D_2H_2)$:

$$\begin{matrix} R_I{\cdot}C{=}NO \\ | \\ R_{II}{\cdot}C{:}NOH \end{matrix}\!\!>\!M\!<\!\!\begin{matrix} NO{=}C{\cdot}R_I \\ | \\ NOH{:}C{\cdot}R_{II} \end{matrix},$$

is adduced.

According to this formula the dioximines are cyclic compounds, and belong to the inner complex salts.

208. "The chlorination and bromination of substituted toluenes."
By Julius Berend Cohen and Colin James Smithells. (Trans., 1914, 1907.)

In former papers by Cohen and Dakin (T., 1901, **79**, 1111) and Cohen and Dutt (T., 1914, **105**, 501) it has been shown that the orienting effect of *o*-chlorotoluene on chlorination is very different from that of *o*-bromotoluene on bromination, and it was thought desirable to determine the influence of *o*-chlorotoluene on bromination and of *o*-bromotoluene on chlorination. At the same time the

other chloro- and bromo-toluenes have been included in the present inquiry.

The results are tabulated alongside those of the two former investigations:

Chlorination.

Bromotoluene.	Products.	Chlorotoluene.	Products.
Ortho	2 : 4, 2 : 6	Ortho	2 : 4, 2 : 3, 2 : 6, (2 : 5)
Meta	2 : 5, 3 : 4	Meta	2 : 5, 3 : 4
Para	2 : 4, 3 : 4	Para	2 : 4, 3 : 4

Bromination.

Chlorotoluene.	Products.	Bromotoluene.	Products.
Ortho	2 : 5, 2 : 4	Ortho	2 : 5, 2 : 4
Meta	2 : 5, 3 : 4	Meta	2 : 5, 3 : 4, (3 : 5)
Para	2 : 4, 3 : 4	Para	2 : 4, 3 : 4

It will be seen from the above table that the principal difference in the behaviour of the isomerides lies in the relative quantity and character of the products derived from the ortho-compounds, more especially if a comparison is made between the products of chlorination and bromination. The authors do not attempt to explain these irregularities.

209. "The action of cold concentrated hydrochloric acid on starch and maltose." By Arthur John Daish. (Trans., 1914, 2053.)

The hydrolysis of starch and maltose by cold fuming hydrochloric acid (D^{15} 1·210) has been studied. In the case of starch it is probable that, as with diastatic enzymes, soluble starch, dextrin, and maltose are formed in succession, but these stages are passed through very rapidly, so that after 135 minutes 86 per cent. of the theoretical quantity of dextrose has been formed. Maltose is hydrolysed to dextrose not much more rapidly than starch itself, so that although fuming hydrochloric acid decomposes starch to maltose with extreme rapidity, the production of dextrose is limited by the rate of the hydrolysis of maltose. The essential similarity of the action of acids and enzymes, especially of taka-diastase, on starch is discussed. It is concluded that in both cases the dextrose which is formed as the final product is derived from maltose produced as an intermediary (Davis, *J. Soc. Dyers*, 1914, **30**, 249).

It is shown that, contrary to the opinion expressed by Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401), when dextrose is dissolved in ordinary concentrated or fuming hydrochloric acid, a certain amount of synthetic action always occurs, even when only 1 per cent. of the sugar is present. This is made evident by a

gradual rise of the specific rotatory power, and a corresponding falling off of the cupric reducing power. In the case of the fuming acid the gradual destruction of dextrose is liable to mask this effect, but in ordinary concentrated hydrochloric acid, when the destruction of dextrose takes place far more slowly, it is very apparent.

210. "The velocity of hydrolysis of starch and maltose by cold concentrated and fuming hydrochloric acid." By Arthur John Daish. (Trans., 1914, 2065.)

The velocity of hydrolysis of starch and maltose has been studied polarimetrically at 20·0°, and a comparison has been made with the results obtained on studying the action of enzymes on starch and maltose. It is shown in the case of maltose that the action of fuming hydrochloric acid gives a velocity-coefficient which is practically constant throughout the change, the extreme range being only about 3 per cent. (0·0103 to 0·0106). The action is practically unimolecular. With soluble starch the velocity-coefficient is not constant, but rises continually during the hydrolysis (0·0052 to 0·0063), the variation being about 20 per cent. In this case the departure from the unimolecular law is due to the change taking place in successive stages.

The results obtained with ordinary concentrated hydrochloric acid and either maltose or soluble starch are similar to those obtained when enzymes act on these substances; that is to say, the velocity-coefficient calculated by a logarithmic equation is not constant, but shows considerable variation during the action. These results and the departure of the law of action of enzymes from a simple law are best explained by the view put forward by Davis (*J. Soc. Dyers*, 1914, **30**, 249) that in such cases a number of successive changes take place; this necessarily influences the velocity-coefficient when calculated in the ordinary way.

The action of fuming hydrochloric acid on cellulose, recently studied by Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401), is an extreme instance of an action occurring in successive stages.

211. "The osmotic pressure and physical constitution of caoutchouc solutions." By William Augustus Caspari. (Trans., 1914, 2139.)

The author has made a study of the osmotic rises exhibited against pure solvent by benzene and light petroleum solutions of caoutchouc. A convenient apparatus is described, in which the semipermeable septum consists of a cylindrical cell of porous earthenware impregnated with cold-vulcanised caoutchouc.

It is found that the osmotic rise, in the case of viscid solutions, is not proportional to the concentration, but increases much more rapidly than the same. Of solutions having the same concentration but different viscosities, the more viscous shows a higher rise than the less viscous. The conclusion is drawn that the osmotic rise is not due to pure osmotic pressure as ordinarily understood, but depends also on the physical nature of the solution, and it is sought to explain the phenomena by the hypothesis that the solutions consist of an elastic gel-phase dispersed in a sol-phase.

So far as the experiments permit of any conclusion as to the molecular weight of caoutchouc in solution, they point to a very high value, of the order of 100,000. A lower value, namely, 40,000, is indicated for gutta-percha in solution.

212. "Studies in phototropy and thermotropy. Part V. Polymorphic 4-hydroxybenzylidenearylamines produced by trituration and by the influence of sunlight." By Alfred Senier and Robert Benjamin Forster. (Trans., 1914, 2462.)

Various 4-hydroxybenzylidenearylamines were prepared and examined in the hope of discovering further instances of phototropic and thermotropic phenomena amongst the members of a class of compounds in which trituration-dimorphism had already been detected (Senier and Shepheard, T., 1909, **95**, 1951, 1954).

It is incidentally found that dimorphism effected by trituration is a general character of 4-hydroxybenzylidenearylamines, and, further, that their behaviour in this respect is parallel to that of mercuric iodide, which below 126° changes by trituration from its yellow to its red dimorphic variety.

Most of the compounds examined are thermotropic, and some exhibit phototropy, and in most cases a third polymorphic form is produced by the prolonged action of actinic light.

213. "The condensation of furan-2:5-dialdehyde with malonic ester and malonic acid." By William Francis Cooper and Walter Harold Nuttall. (Trans., 1914, 2218.)

Furan-2:5-dialdehyde condenses with two molecules of ethyl malonate, forming *ethyl furan-2:5-dimethylenemalonate*, which, on hydrolysis, gives the corresponding *acid*. This acid forms two peculiar isomeric additive compounds with acetic acid. On crystallising the yellow tetracarboxylic acid from glacial acetic acid, a brown pentabasic acid results, which is a compound of one molecule of the original tetracarboxylic acid with one molecule of acetic

acid. The other additive pentabasic compound of the two acids, isomeric with the above but red in colour, is obtained when furan-2:5-dialdehyde is condensed with malonic acid, using glacial acetic acid as catalyst.

The only difference between the isomerides is apparently one of colour, which is not affected by repeated recrystallisation from glacial acetic acid.

On esterification, all three acids, namely, the yellow tetracarboxylic, and the brown and red pentabasic acids, give the same ethyl furan-2:5-dimethylenemalonate, which is identical with that obtained by the direct condensation of furan-2:5-dialdehyde with ethyl malonate.

On condensing furan-2:5-dialdehyde with malonic acid in the presence of pyridine, a brown, amorphous product results, which is probably a mixture of stereoisomerides of *furan-2:5-diacrylic acid*. It gives a crystalline ester on esterification with ethyl alcohol, whilst, on reduction with sodium amalgam, *furan-2:5-dipropionic acid* is formed. If the reduction is carried out with aluminium filings, an intermediate acid, containing two atoms of hydrogen less than the dipropionic acid, results.

214. "Catalysis. Part XVIII. The reactions of both the ions and the molecules of acids, bases, and salts; the reactions of alkyl haloids with phenoxides and ethoxides." By John Hanston Shroder and Solomon Farley Acree.

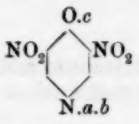
The older work of Hecht, Conrad, and Brückner and the recent investigations by Segaller show that the velocities of the reactions of alkyl haloids with phenoxides and ethoxides can be expressed by the purely empirical equation, (1) $K'_N = K_N + a \log (V'/V)$. All this work can, however, be interpreted in terms of Acree's theory that both the ethoxide (phenoxide) ions and the non-ionised ethoxide (phenoxide) react with the alkyl haloids according to the equations (2) $K_N = K_i + K_n(1-\alpha)$, (3) $K'_N = K_i + K_m(1-\alpha')$, etc. The empirical equation (1) holds, therefore, because the experimental data give approximate constants for "a" in the equation (4), $a = \alpha' - \alpha/\log (V'/V)$, derived from a comparison of equations (1), (2), and (3), and (1) becomes practically identical with (2) and (3).

215. "Synthetical experiments in the group of the *iso*quinoline alkaloids. Part IV. The synthesis of β-gnoscopine." By Edward Hope and Robert Robinson. (Trans., 1914, 2085.)

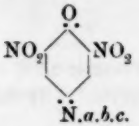
A detailed description of work of which a preliminary account has already appeared (P., 1912, **28**, 16).

216. "Quinone–ammonium derivatives. Part IV. Products of the extreme alkylation of alkylated *iso*picramic acid." By Raphael Meldola and William Francis Hollely. (Trans., 1914, 2073.)

The alkylation of mono- and di-methyl*iso*picramic acid and of mono- and di-benzyl*iso*picramic acid by methyl and ethyl sulphate under various conditions has led to the conclusion that in most cases the two isomeric compounds I and II are formed simultaneously. Of these I represents a phenolic ether (anisidine or phenetidine derivative), and II a true quinone–ammonium compound. A member of the latter series containing an asymmetric nitrogen atom in which *a*, *b*, and *c* stand respectively for methyl, ethyl, and benzyl has been prepared.



(I.)



(II.)

217. "Organo-derivatives of bismuth. Part I. The preparation and properties of some tertiary aromatic bismuthines and their halogen derivatives." By Frederick Challenger. (Trans., 1914, 2210.)

The interaction of triphenylbismuthine dibromide and magnesium phenyl bromide in ethereal solution does not give tetraphenylbismuthonium bromide, but derivatives of tervalent bismuth seem to be exclusively produced, triphenylbismuthine, diphenylbromobismuthine and phenyldibromobismuthine being isolated from the reaction mixture.

When treated with magnesium ethyl bromide, triphenylbismuthine dibromide gives triphenylbismuthine, diphenylbromobismuthine and bromobenzene.

The instability of the bismuthonium haloids is also shared to a less extent by the bismuthine dibromides, for example, triphenylbismuthine dibromide loses bromobenzene on boiling its solution in benzene, diphenylbromobismuthine being obtained.

When diphenylbromobismuthine reacts with magnesium α-naphthyl bromide, *diphenyl-α-naphthylbismuthine* is produced. This melts at 119°, and forms a yellow, crystalline *dibromide*, melting at 140°.

Tri-α-naphthylbismuthine (P., 1913, **29**, 76) also forms a yellow *dibromide* melting at 120°.

On attempting to prepare diphenylethylbismuthine by the interaction of diphenylbromobismuthine and magnesium ethyl bromide an unexpected result was obtained, triphenylbismuthine and triethylbismuthine being produced.

Phenyldibromobismuthine, which forms yellow needles melting at 206°, is obtained by the action of bromine on diphenylbromobismuthine, both in chloroform solution. Bromobenzene is split off, and if excess of bromine is employed some bismuth bromide is obtained.

218. "*p*-Toluoylacetic acid, *o*-nitro-*p*-toluoylacetic acid, and 6:6″-dimethylindigotin." By James Cooper Duff. (Trans., 1914, 2182.)

Founded on the work of Needham and Perkin on *o*-nitrobenzoylacetic acid (T., 1904, **85**, 148), which acid has since been found to give indigotin when reduced with dilute sodium hydroxide solution and zinc dust, the preparation of the corresponding nitro-*p*-toluoylacetic acid has been undertaken. *o*-Nitro-*p*-toluoyl chloride is condensed with ethyl acetoacetate, whereby *ethyl* o-*nitro*-p-*toluoylacetate* is obtained in colourless plates. On hydrolysis the ester yields o-*nitro*-p-*toluoylacetic acid*, which when dissolved in dilute sodium hydroxide solution and warmed gives 6:6″-*dimethylindigotin*.

The preparation of ethyl *p*-toluoylacetate and *p*-toluoylacetic acid from *p*-toluoyl chloride and ethyl acetoacetate is also described.

219. "The dissociation of gaseous nitrogen trioxide." By Bernard Mouat Jones. (Trans., 1914, 2310.)

The vapour density of dry nitrogen trioxide has been determined at a series of temperatures, pressures, and volumes, varying from 15° to 139° and 106 mm. to 818 mm. The densities obtained vary from 35·07 to 24·00 (H = 1). The numbers obtained agree fairly closely with the assumption that the "dry" nitrogen trioxide dissociated according to the equation:

$$N_4O_6 \rightleftharpoons N_2O_3 + NO_2 + NO \quad . \quad . \quad . \quad . \quad . \quad (a),$$

this dissociation being nearly complete at 140°, and the nitrogen trioxide not dissociating further. At the same time owing to incomplete drying there are present some "wet" NO_2 (and N_2O_4) and NO molecules which do not unite to give nitrogen trioxide or take part in equation (*a*), which is only concerned with "dry" molecules.

The dissociation constant for equation (*a*) at different temperatures has been calculated:

$$K = \frac{C_{N_4O}}{C_{N_2O_3}C_{NO_2}C_{NO}} \cdot V^2,$$

and the values obtained indicate that at temperatures in the neighbourhood of the boiling point (+3°) the trioxide consists mainly of N_4O_6, and the blue colour of the very dry liquid as compared with the green colour of ordinary "wet" specimens is accounted for.

220. "The volumetric determination of carbon in aliphatic substances in the wet way." By Egerton Charles Grey. (Trans., 1914, 2204.)

A method is described for the determination of total carbon, which is based on the oxidation of the substance by potassium dichromate and phosphoric acid to carbon dioxide or a mixture of carbon monoxide and acetic acid. The carbon dioxide is measured, and the acetic acid is distilled from the residual fluid and titrated with *N*/30-baryta. The method gives accurate results.

When the substance is oxidised quantitatively to carbon dioxide only 2 or 3 centigrams need be used, but about a decigram is required when acetic acid has to be determined.

The acetic acid is formed from substances containing the methyl group in the chain, and the method therefore gives simultaneously some indication of the constitution of the substance.

With a modification of the apparatus described, the method would be well adapted to microchemical analysis.

Ethyl alcohol is oxidised practically quantitatively to acetic acid, and may be accurately determined in dilute solutions by this method.

The analyses of several typical aliphatic substances are given.

221. "Investigations on the dependence of rotatory power on chemical constitution. Part VII. Some normal esters of the carbinols of the formula $C_2H_5{\cdot}CH(OH){\cdot}R$." By Joseph Kenyon. (Trans., 1914, 2226.)

The fourteen members of the "ethyl" series of carbinols of the general formula $C_2H_5{\cdot}CH(OH){\cdot}R$, which were described in Part IV, have been converted into the corresponding *acetates* and n-*heptoates*. Whereas the carbinols exhibited special exaltations in rotatory power at the positions where the growing chain contained five and six and also ten and eleven carbon atoms, it is found

that the rotatory powers of the corresponding acetates show this special exaltation to only a very slight extent.

In addition, fourteen normal *esters* (from the *acetate* to the *stearate*) of *d*-γ-nonanol have been prepared, and their rotatory values determined at temperatures up to 200° for light of three different wave-lengths. As the series is ascended it is found that there are special exaltations in molecular rotatory power at the positions where the number of carbon atoms in the growing acyl group is five and ten and eleven respectively.

When the molecular rotatory powers of these esters are determined in 5 per cent. ethyl-alcoholic solution it is found that these special exaltations are non-existent, whilst when the determinations are made in carbon disulphide solution the exaltations give place to depressions.

222. "Investigations on the dependence of rotatory power on chemical constitution. Part VIII. The optical rotatory powers of the normal esters of methylbenzylcarbinol." By Joseph Kenyon and Robert Howson Pickard. (Trans., 1914, 2262.)

Fourteen normal esters (from the acetate to the stearate) of *d*-methylbenzylcarbinol have been prepared, and their rotatory powers determined at temperatures up to 200° for four different wave-lengths. As the series is ascended, the molecular rotatory powers increase, the regularity of the increment being interrupted by a special exaltation exhibited by the *n*-valerate. The "temperature-rotation" coefficients decrease on ascending the series, but the curves for the acetate and propionate exhibit a region of "anomalous" rotatory dispersion at and above 140°, whilst in 5 per cent. solutions in carbon disulphide the rotatory powers of all the esters have a different sign from those exhibited in the homogeneous state.

All observations of the rotatory power of *d*-methylbenzylcarbinol and these fourteen esters can be correlated on one "characteristic diagram."

223 "Experiments on the conversion of certain dibromides of the type of ethylene dibromide into the corresponding glycols." By Ernest Graham Bainbridge. (Trans., 1914, 2291.)

The author has found that glycol diacetate can be hydrolysed by boiling with a dilute alcoholic solution of sodium ethoxide, a yield of 85 per cent. of the theoretical being readily obtainable. Investigations were also carried out with dilute alcoholic solutions

of sodium hydroxide and sodium acetate. Hydrolysis was effected by means of these agents, but the yields were smaller than in the case of sodium ethoxide.

This method of hydrolysis proved successful with the diacetates of trimethyleneglycol and αγ-butylene glycol. Propylene glycol diacetate and ψ-butylene glycol diacetate cannot be hydrolysed by this means.

The author has also investigated the action of certain metallic acetates on dibromides, and finds that propylene bromide, *iso*-butylene bromide, and ψ-butylene bromide are partly converted into α-bromo-Δ^{α}-propylene, α-bromo-β-methyl-Δ^{α}-propylene and β-bromo-ψ-butylene respectively.

224. "The metallography of German silver." By Frank Charles Thompson. (Trans., 1914, 2342.)

As a result of the employment of the "principle of maximum work" and of high-power microscopic examination, there is reason to believe that the oxygen present in commercial German-silver is present as exceedingly finely divided zinc oxide.

Deoxidants, for example, manganese and aluminium, exert marked influence in refining the structure of these alloys when annealed after cold working.

As the amount of nickel in the German silver is increased, the size of the crystals for the same treatment by heat becomes much finer, and at the same time the tendency for the "as cast" structure to persist despite thermal and mechanical treatment is increased.

By overheating German-silver a new dendritic structure is developed, and crystal twinning may be almost entirely removed.

In alloys containing an appreciable percentage of lead or tin respectively, free lead and a material which is probably a copper–tin compound are found.

225. "Electromotive forces in alcohol. Part IV. Combinations of the hydrogen and calomel electrodes." By Reginald Furness, Robert Taylor Hardman, and Edgar Newbery. (Trans., 1914, 2302.)

The electromotive forces of various combinations of the hydrogen electrode with the calomel electrode have been determined, anhydrous alcohol being used throughout. The effects of the addition of sodium and lithium chlorides to the cell-liquid of the hydrogen electrode in alcoholic hydrogen chloride, and also that of the

addition of small quantities of hydrogen chloride to the cell-liquid of the calomel electrode in alcoholic sodium and lithium chlorides, have also been made. Finally, electromotive forces of combinations containing saturated alcoholic solutions of sodium chloride in both compartments have been determined.

From an analysis of the numbers obtained it may be concluded that the hydrogen electrode gives nearly correct results in alcoholic hydrogen chloride, as is also the case with the calomel electrode in dilute alcoholic sodium chloride. In the presence of alcoholic hydrogen chloride, however, all measurements with the calomel electrode are untrustworthy.

The potential attained by the hydrogen electrode in $N/500$-alcoholic hydrogen chloride appears to be about 6 millivolts below the theoretical value.

226. "The influence of solvents on the rotation of optically active compounds. Part XX. Isomeric solvents." By Thomas Stewart Patterson and Ernest Ferguson Pollock. (Trans., 1914, 2322.)

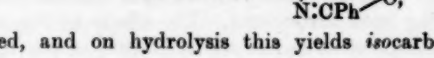
The rotations of *iso*butyl malate and of ethyl tartrate have been examined in a number of different solvents, and the results are discussed in connexion with the various types of isomerism.

227. "Some derivatives of ortho-vanillin." By William Henry Perkin, jun., and Robert Robinson. (Trans., 1914, 2376.)

The authors have prepared the benzoic acid, benzyl alcohol, cinnamic acid, phenylpropionic acid, hydrindone, and other simple derivatives of the *o*-vecatric series. The condensation of *o*-veratraldehyde with ethyl cyanoacetate leads to the production of *8-methoxycoumarin-3-carboxylic acid*, and by the nitration of the aldehyde, *6-nitro-o-veratraldehyde* is produced, which furnishes *4 : 5 : 4′ : 5′-tetramethoxyindigotin*.

228. "Some derivatives of *iso*coumarin and *iso*carbostyril." By David Bain, William Henry Perkin, jun., and Robert Robinson. (Trans., 1914, 2392.)

By the condensation of methyl phthalaldehydrate with hippuric acid, *2-phenyl-4-o-carboxymethylbenzylideneoxazolone*,



is formed, and on hydrolysis this yields *iso*carbostyrilcarboxylic acid.

By an analogous method the authors have prepared 7:8-dimethoxy*iso*carbostyril, from which *iso*oxyberberine is derived.

ω-Opianoylacetophenone, prepared from silver opianate and *ω-bromoacetophenone*, when treated with alkaline condensing agents, yields 3-*benzoyl*-7:8-*dimethoxy*isocoumarin, but when potassium opianate is condensed with ω-bromoacetophenone, *ω-benzoylbromomethylmeconine* is formed, which, on treatment with alkalis, also yields 3-benzoyl-7:8-dimethoxy*iso*coumarin.

229. "Diketo-5:6-dimethoxyhydrindene." By William Henry Perkin, jun., Walter Morrell Roberts, and Robert Robinson. (Trans., 1914, 2405.)

The method previously described for producing 1:2-diketohydrindene (T., 1912, **101**, 232) by the hydrolysis of *iso*nitroso-1:2-diketohydrindene with formaldehyde and hydrochloric acid has now been applied to the preparation of 1:2-*diketo*-5:6-*dimethoxyhydrindene* and 1:2-*diketo*-5:6-*methylenedioxyhydrindene*.

230. "Overvoltage." By Edgar Newbery. (Trans., 1914, 2419.)

It has been shown that during the electrolysis of an acid solution with metal electrodes the gas before liberation penetrates the metal surface, and on emerging breaks open the surface. If a colloid is present, some of it is carried into the metal along with the gas.

The presence of a colloid in all cases raises the hydrogen overvoltage of a metal, and diminishes the degree of ionisation of the gas liberated. The overvoltage during deposition of a metal is affected to a much smaller degree.

The overvoltage of the metal and the ionisation of the gas liberated show an inverse relationship.

The overvoltage of a metal is determined by three factors, namely, (1) supersaturation of the electrodes with gas in the molecular condition, the accumulation of this gas being brought about through the permeability of the metal to ions, and the inability of the free gas to escape except by solution or breaking the metal surface; (2) deficiency or excess of non-hydrated ions in the immediate neighbourhood of the electrodes; and (3) inductive action of the escaping ionised gas on the electrodes.

Under certain conditions the third factor is sufficiently powerful to reduce the measured overvoltage of a metal to a negative quantity.

231. "Adiabatic and isothermal compressibilities of liquids between one and two atmospheres' pressure." By Daniel Tyrer. (Trans., 1914, 2534.)

The method of determining the adiabatic compressibility of a liquid, described in a previous paper (T., 1913, **103**, 1675) has been modified and improved. Extended measurements have been made for various liquids over fairly wide ranges of temperature. Results for eighteen liquids have now been completed. From the results values of the ordinary isothermal compressibility β have been calculated by aid of the following thermodynamical equation:

$$\beta = \alpha + \frac{T\left(\frac{dv}{dt}\right)^2}{Jv C_p},$$

where α is the adiabatic compressibility, v the specific volume, J the mechanical equivalent of heat, and C_p the specific heat at constant pressure.

In addition, for each liquid, accurate determinations of the specific volume at different temperatures have been made, and from the results values of dv/dt have been calculated for use in the above equation. It has been found that the results of many early investigators, among whom may be mentioned Quincke (*Ann. Phys. Chem.*, 1883, [iii], **19**, 401) and Grassi (*Ann. Chim. Phys.*, 1851, [iii], **31**, 437), are really adiabatic and not isothermal, as supposed by their authors and as entered in various physico-chemical tables. They agree well with the present determinations of the adiabatic compressibility, and are altogether discordant with the isothermal results.

232. "The colouring matters of Rhamnus catharticus." By Josef Oesch and Arthur George Perkin. (Trans., 1914, 2280.)

According to Tschirch and Polacco (*Arch. Pharm.*, 1900, **238**, 459), the berries of *R. catharticus* contain (as glucoside) the yellow colouring matters rhamnocitrin, $C_{13}H_{10}O_5$, rhamnolutin, $C_{15}H_{10}O_6$, rhamnochrysin, $C_{13}H_{10}O_7$, and β-rhamnocitrin, $C_{13}H_{10}O_5$, in all of which methoxy-groups are absent. Krasowski (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1510), on the other hand, could isolate only rhamnetin and quercetin, and considered that rhamnolutin is possibly rhamnetin, whereas rhamnocitrin is exactly like quercetin and rhamnetin. Again, instead of rhamnochrysin, a mixture of quercetin and emodin was obtained. The results of the present investigation show that rhamnocitrin, $C_{16}H_{12}O_6$, is a monomethyl ether of kæmpferol; that rhamnolutin, $C_{15}H_{10}O_6$, the main colour-

ing matter, is kæmpferol, whereas β-rhamnocitrin present in small amount is rhamnetin, $C_{16}H_{12}O_7$. Incidentally, it was found that pure acetylrhamnetin melts at 190—192°. As indicated by Krasowski, quercetin can also be obtained from these berries, but the amount detected was trifling. The presence of a substance corresponding with rhamnochrysin could not be confirmed.

233. "The constituents of the flowers of Matricaria Chamomilla." By Frederick Belding Power and Henry Browning, jun. (Trans., 1914, 2280.)

The material employed for this investigation consisted of the flower-heads of *Matricaria Chamomilla*, Linné.

In addition to a deep blue essential oil, which deposited a very small amount of umbelliferone methyl ether, the flowers were found to contain the following compounds: (i) salicylic acid, together with, apparently, an octoic acid; (ii) apigenin, $C_{15}H_{10}O_5$; (iii) a glucoside of apigenin, which could not be obtained in a crystalline state; (iv) umbelliferone methyl ether, $C_{10}H_8O_3$, and a crystalline product (m. p. 237—239°) which possessed the characters of a mixture of umbelliferone and a dihydroxycoumarin; (v) choline, $C_5H_{15}O_2N$; (vi) triacontane, $C_{30}H_{62}$; (vii) a phytosterol, $C_{27}H_{46}O$; (viii) a phytosterol glucoside, $C_{33}H_{56}O_6$; (ix) palmitic, stearic, cerotic, oleic, and linolic acids, together with an indefinite mixture of volatile fatty acids. The flowers contained, furthermore, a quantity of sugar which yielded *d*-phenylglucosazone (m. p. 208°). The fatty and resinous material, from which some of the above-mentioned substances were obtained, amounted to 5·9 per cent. of the weight of flowers employed.

234. "Hydrogen potentials of mixtures of acetic acid and sodium acetate." By George Stanley Walpole. (Trans., 1914, 2501.)

The extremely small contact potential between mixtures of acetic acid and sodium acetate and solutions of potassium chloride renders them particularly suitable for electrometric investigation.

Hydrogen potential measurements, corrected for this small potential difference by Bjerrum's extrapolation method, have been made of a series of these mixtures against the *N*/10-calomel electrode. With these have been compared the calculated results obtained by the well known energy relationship and Fels' original equation. By the introduction of three rational corrections to this equation, one of them based on the principle of isohydrism, calculated results have been obtained agreeing with those observed to within

1·5 millivolts or less over the whole range from pure acetic acid to a mixture containing thirty-two times as much sodium acetate as acetic acid. The original equation is less accurate than the new equation for solutions containing much sodium acetate, and is inaccurate for mixtures approximating to pure acetic acid in composition. For pure acetic acid Fels' equation is indeterminate, whereas the new equation simplifies to the correct expression for the hydrion concentration of acetic acid in terms of its dissociation constant and its concentration.

An electrometric method of standardising sodium acetate capable of development to a high order of accuracy has been devised. Using this method the hydrogen potential of the "standard acetate" solution of Michaelis can certainly be reproduced to within ±0·10 millivolt, and probably with even a higher order of accuracy.

235. "The effect of dilution on the hydrogen potentials of acetic acid and 'standard acetate' solutions." By George Stanley Walpole. (Trans., 1914, 2521.)

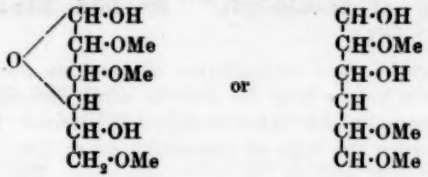
The relationship between the hydrogen potential of acetic acid and the logarithm of its dilution is strictly linear. A similar relationship does not hold for "standard acetate."

The electrode potential of moist hydrogen at 760 mm. pressure in "standard acetate" against the *N*/10-calomel electrode at 18° has been re-determined. The result is 0·6046 volt with saturated potassium chloride solution interposed between the two halves of the cell; corrected for contact potential it is 0·6045 volt. This value agrees to the fourth decimal place with those obtained by Sörensen and by Michaelis.

236. "The methylation of cellulose. Part II. Hydrolysis of methylated cellulose." By William Smith Denham and Hilda Woodhouse. (Trans., 1914, 2357.)

Further experiments have shown that on the methylation of cellulose by means of sodium hydroxide and methyl sulphate in the manner already described (T., 1913, **103**, 1735), the substitution probably does not occur uniformly. This conclusion is supported by a study of the products obtained on hydrolysing the methylated cellulose by means of a very concentrated solution of hydrogen chloride in water. The chief products isolated were monomethyl glucose and dimethyl glucose, both in the amorphous state and probably mixtures of isomeric substances, and a crystal-

line trimethyl glucose. The monomethyl glucose and dimethyl glucose form osazones. From the fact that the trimethyl glucose does not form an osazone, and from a comparison of its properties with those of trimethyl glucoses of known constitution prepared by Irvine and his collaborators, the formula for the trimethyl glucose derived from methylated cellulose must be either



237. "The reaction of *p*-benzoquinone with sulphurous acid and with alkali. Part I." By John Wallis Dodgson. (Trans., 1914, 2435.)

The usual explanation of the reaction which takes place when *p*-benzoquinone is reduced with sulphurous acid is expressed by the equation:

$$C_6H_4O_2 + SO_2 + H_2O \longrightarrow C_6H_4(OH)_2 + H_2SO_4.$$

Sheppard and Mees (*Zeitsch. wiss. Photochem.*, 1902, **2**, 5) suggested also the formation of dithionic acid:

$$C_6H_4O_2 + 2SO_2 + 2H_2O \longrightarrow C_6H_4(OH)_2 + H_2S_2O_6.$$

The author has found that dithionic acid, if produced at all, is formed in very minute quantities, and that whereas about 80 per cent. of *p*-benzoquinone is reduced to quinol with the accompanying oxidation of the sulphurous acid to sulphuric acid, the remainder almost entirely forms quinolsulphonic acid.

The effect of change of temperature on the reactions is inconsiderable, but the presence of much hydrochloric acid almost entirely inhibits both reactions owing to the formation of chloroquinol.

The effect of the addition of alkali is remarkable. In experiments on this point, the *p*-benzoquinone solution was mixed with sulphurous acid to which varying amounts of sodium hydroxide had been added. As long as the amount of alkali used did not exceed that required for the formation of sodium hydrogen sulphite, the result of the reaction, as regards the proportion of sulphate to sulphonate, was practically the same as if sulphurous acid alone had been employed, but the slightest excess caused an immediate and great increase in the amount of sulphonate produced, whilst the yield of sulphate sank to a very small and almost constant quantity.

Further addition of alkali caused a decrease in the amount of sulphonate owing to the action of the alkali on the *p*-benzoquinone.

238. "The absorption spectra of the vapours and solutions of various derivatives of benzaldehyde." By John Edward Purvis. (Trans., 1914, 2482.)

The investigation is a continuation of previous work, and the special aim was to see how far and in what directions various isomeric compounds and other compounds derived from benzaldehyde influence the type of absorption when they are in the vaporous condition and in alcoholic solution. The substances examined were: *o*-, *m*-, and *p*-chlorobenzaldehydes, *o*-, *m*-, and *p*-tolualdehydes, *o*-, *m*-, and *p*-hydroxybenzaldehydes, anisaldehyde, *o*-, *m*-, and *p*-phthalaldehydes, cuminaldehyde, vanillin, benzaldoxime, benzylidene chloride, benzaldehyde sodium hydrogen sulphite, mandelonitrile, benzoyl chloride, and cinnamaldehyde.

239. "The isomerism of the oximes. Part V. *m*-Methoxybenzaldoxime, vanillinoxime and veratraldoxime." By Oscar Lisle Brady and Frederick Percy Dunn. (Trans., 1914, 2409.)

In connexion with their work on the underlying causes of the isomerism of the oximes, the authors have investigated three more oximes and some of their derivatives. Whilst there is some evidence that *m*-methoxybenzaldoxime, like anisaldoxime, exists in *anti*- and *syn*-forms, vanillinoxime and veratraldoxime show no sign of giving a second isomeride. This is in accordance with the authors' previous experience.

The position of the acetyl group in acetyl-*m*-methoxybenzaldoxime and in monoacetylvanillinoxime has been determined; in each case the oximino- and not the phenolic hydroxy-group is acetylated.

240. "Photokinetics of sodium hypochlorite solutions. Part II." By Leo Spencer. (Trans., 1914, 2565.)

The present investigation is a continuation of that of W. C. McC. Lewis (T., 1912, **101**, 2371) on the decomposition of sodium hypochlorite into sodium chloride and oxygen under the action of the rays from a uviol lamp. A modified form of apparatus has been employed, by means of which it has been possible to keep the temperature of the solution constant to 1°. Velocity-constants have

been determined for the full lamp, and for five definite spectral regions extending from $\lambda 578\mu\mu$ to $\lambda 313\mu\mu$. The results obtained bear out Luther's absorption theory of photochemical action. The temperature-coefficient of the reaction has been determined, and is shown to be very small. Further, it has been found that the uviol light slightly accelerates the bleaching action of sodium hypochlorite on linen.

241. "Sodium amalgams: specific volumes and electrical conductivities." By Ernest Vanstone.

When specific volumes of solid amalgams are plotted against concentrations expressed in percentages by weight, a curve is obtained which shows many discontinuities, indicating the existence of intermetallic compounds.

The agreement with the results of the thermal method is satisfactory. When the specific volumes of liquid amalgams are plotted, a straight line is obtained, showing that intermetallic compounds do not exist in the liquid condition at the temperatures of the experiments, namely, 110°, 184°, and 237°.

The electrical conductivities of liquid amalgams have been determined at 110° and 135°.

The conductivity-concentration diagram consists of a smooth curve, thus confirming the results of the experiments on specific volume, that intermetallic compounds do not exist in the liquid condition.

242. "Electromotive forces in alcohol. Part V. The dropping electrode in alcoholic solutions." By Edgar Newbery. (Trans., 1914, 2553.)

The author has carefully examined the behaviour of the dropping electrode in absolute alcoholic solutions, the apparatus devised by Palmaer (*Zeitsch. Elektrochem.*, 1903, **9**, 755) being used with certain modifications which were found necessary. Solutions of sodium chloride containing sodium cyanide, mercuric cyanide, sodium and hydrogen sulphides were used as "null" solutions against the calomel electrode in alcoholic sodium chloride.

Very constant and reproducible results were obtained with various null solutions, but these are shown to be inconsistent with one another and with the theory of the dropping electrode.

243. "Magnesium boride and amorphous boron."
By Rames Chandra Ray. (Trans., 1914, 2162.)

Amorphous boron was prepared by heating in a current of hydrogen a mixture of magnesium and boron trioxide or fused borax in varying proportions. After freeing the heated mixture from the admixed impurities, and after washing the residue and drying it in a vacuum, a greyish-red powder was obtained. This so-called amorphous boron was always found to contain much oxygen, thus confirming Weintraub's experiments. Probably the so-called amorphous boron is a solution in elementary boron, of a lower oxide of boron and of magnesium oxide, possibly in combination as a borite. Boron could be obtained in a state approaching purity in only one form, namely, that of a crystalline substance which is practically insoluble in nitric acid.

On heating crystalline boron with magnesium no reaction took place. When a mixture of 1 part of boron trioxide with $2\frac{1}{4}$ parts of magnesium powder was heated to a red-heat in a current of hydrogen for forty-five minutes, a mixture of magnesium boride (Mg_3B_2) and oxide in the theoretical proportions was obtained. A similar mixture was also obtained on heating the so-called amorphous boron with magnesium. From the results of analyses it was proved that at a red-heat and under normal pressure only one boride, having the formula Mg_3B_2, is formed. On heating the boride magnesium was driven off, and the greater part of the boron separated in the crystalline form.

244. "Diphenyl-2 : 3 : 2′ : 3′- and -3 : 4 : 3′ : 4′-tetracarboxylic acids."
By James Kenner and Annie Moore Mathews. (Trans., 1914, 2471.)

An account having been given of the preparation and reactions of *diphenyl-2 : 3 : 2′ : 3′-tetracarboxylic acid*, it is suggested that the results favour the usual formula for diphenyl rather than that proposed by Kaufler. Additional evidence is also adduced in favour of the explanation previously advanced of the ready formation of dibenzo*cyclo*heptadiene derivatives from those of 2 : 2′-dimethyldiphenyl (Kenner and Turner, T., 1911, **99**, 2101; Kenner, T., 1913, **103**, 615).

Tetramethyl diphenyl-3 : 4 : 3′ : 4′-tetracarboxylate was prepared from *dimethyl 4-iodophthalate*, and its properties, as well as those of the tetracarboxylic acid, are shown to agree in the main with those of a diphenyltetracarboxylic acid prepared by Liebermann (*Ber.*, 1912, **45**, 1187). The constitution of the latter compound was therefore decided.

245. "The composition of coal. Part II." By David Trevor Jones and Richard Vernon Wheeler. (Trans., 1914, 2562.)

The results of distilling bituminous coal in a vacuum at 350° are described. It is shown that the liquid distillates are similar in character and composition to those obtained from the same coal at 430° (T., 1914, **105**, 140).

The presence in the oils obtained at 350° of aromatic compounds, previously assumed to arise from the decomposition, with elimination of hydrogen, of hydrogenated aromatic nuclei at temperatures not much below 400° (the temperature at which dihydronaphthalene had been found to decompose), is explained by assuming a decomposition analogous to that observed by Cannizzaro (*Gazzetta*, 1884, **13**, 385) in the case of santonous acid which, between 300° and 350°, yields chiefly 1 : 4-dimethyl-5 : 8-dihydro-β-naphthol and propionic acid, hydrogen not necessarily being eliminated.

246. "Investigations on the dependence of rotatory power on chemical constitution. Part IX. The rotatory powers of 1-naphthyl-*n*-hexylcarbinol and its esters." By Joseph Kenyon and Robert Howson Pickard.

dl-1-*Naphthyl*-n-*hexylcarbinol* melts at 41°, and its *hydrogen phthalate* at 102—104°. The latter is readily resolved into its optical isomerides by fractional crystallisation of the brucine salt from acetone. The *d*-carbinol melts at 41°, and in the supercooled state is lævorotatory, exhibiting "anomalous" dispersion. It has a complex dispersive power at temperatures below 180°, but above this temperature the observed optical rotations obey the law of simple dispersion. Ten esters (ranging from the acetate to the *n*-undecoate) of the *d*-carbinol, and also the acetate of *l*-1-naphthylmethylcarbinol, have been prepared, and all possess complex dispersive power (at least) up to a temperature of about 200°.

247. "The atomic weight of mercury." By Herbert Brereton Baker and Walter Henry Watson. (Trans., 1914, 2530.)

Mercury was converted into mercuric bromide by direct treatment with liquid bromine, excess of the latter being removed by heating to 70—80° in a current of dry air. A trace of adsorbed bromine still remaining in the weighed product was expelled by fusion, and determined by passing it into a solution of potassium iodide and titrating with *N*/10-thiosulphate. In nine completed

experiments values ranging from 200·50 to 200·62 were obtained for the atomic weight of mercury, the mean result being:

$$Hg = 200{\cdot}57 \pm 0{\cdot}008.$$

248. "The reduction products of ethyl hydrindene-2:2-dicarboxylate." By James Kenner.

Bouveault and Blanc's method of reduction was applied to the above ester with the object of preparing *ωω'-dihydroxy-2:2-dimethylhydrindene*, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C(CH_2{\cdot}OH)_2$. This compound (m. p. 112·5°) was, however, only produced to the extent of 3 per cent. of the calculated amount, the main product being *2-hydroxymethylhydrindene*, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH{\cdot}CH_2{\cdot}OH$ (m. p. 33°), *2-Bromomethylhydrindene*, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH{\cdot}CH_2Br$ (m. p. 21°), reacted only slowly with ethyl malonate and with potassium phthalimide.

These results are discussed in connexion with the general problem of the stability of compounds containing a quaternary carbon atom, and the attempt is made to supply a theoretical basis for this subject.

249. "Solutions of bromine in water, nitrobenzene, and carbon tetrachloride." By Alfred Francis Joseph.

Determinations have been made of the colour and solution-volume of bromine in the above three solvents. In carbon tetrachloride bromine appears to have the same colour as when in a state of vapour at the same concentration; in nitrobenzene the colour is only about two-thirds, and in water about one-third as intense. The solution-volume (from low concentrations up to 60 grams per litre) increases in each case to a maximum, which is greatest for carbon tetrachloride and least for water.

Bromine mixes freely with nitrobenzene and carbon tetrachloride; the rate of its removal in a current of air is twice as fast from solution in the latter as in the former.

250. "Volatile oil from the leaves of Barosma venusta." By Ernest Goulding and Oswald Digby Roberts.

The leaves of *Barosma venusta*, Eckl. and Zeyh., yield about 2 per cent. of a volatile oil, which has a lemon-yellow colour, a pleasant odour, D_{15}^{15} 0·865, and α_D^{22} +0°47′. The percentage com-

position of the oil is approximately as follows: hydrocarbons, chiefly or entirely myrcene, 43; aldehydes, chiefly or entirely anisaldehyde, 0·5; phenols, 0·2; methylchavicol, 21·4; alcohols, partly linalool (calculated as $C_{10}H_{17}\cdot OH$), 14·3; esters (calculated as $C_{10}H_{17}\cdot OAc$). 2·2; sesquiterpenes, etc., 18·4.

251. "The limits of inflammability of mixtures of methane and air." By Maurice John Burgess and Richard Vernon Wheeler.

The different limits of inflammability of mixtures of methane and air, dependent on the direction in which the flame has to travel, are recorded. The results are as follow:

	Methane, per cent.	
	Lower limit.	Higher limit.
Central ignition in large globe ...	5·6	14·8
Vertical tube, closed at both ends:		
(*a*) Ignition at bottom.....	Not less than 5·4	Not more than 14·8.
(*b*) Ignition at top	6·0	13·4
Horizontal tube, closed at both ends:		
Ignition at one end.....	5·4 (flame travels only along top of tube) / 5·6 (methane all burnt)	14·3

252. "The propagation of flame in "limit" mixtures of methane, oxygen, and nitrogen." By Maurice John Burgess and Richard Vernon Wheeler.

A series of determinations was made of the amounts of methane required to form higher- and lower-limit mixtures with various "atmospheres" ranging between air and a mixture of air and nitrogen containing 13·45 per cent. of oxygen. The results were as follows:

Atmosphere.		Methane, per cent.	
Oxygen.	Nitrogen.	Lower limit.	Higher limit.
20·90	79·10 (air)	5·60	14·82
19·22	80·78	—	12·93
18·30	81·70	—	11·91
17·00	83·00	5·80	10·55
15·82	84·18	5·83	8·96
14·86	85·14	6·15	8·36
13·90	86·10	6·35	7·26
13·45	86·55	6·50	6·70
13·25	86·75	No mixture capable of propagating flame.	

An attempt was made to calculate the heat balances during the spread of flame in these limit mixtures from the general equation:

$$(c'M + c''P)(T' - t) + q = xQ \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It was shown that when methane is the combustible gas the

calculations are complicated by the fact that combustion in the flame is incomplete. It was therefore necessary to obtain samples of the "flame gases" while the flames were travelling through the mixtures. Analyses of these gases showed a regular relationship between the ratios O_2/CH_4 in the original mixtures and the proportions of methane that burned completely to form carbon dioxide and steam. The opinion is advanced that the essential reaction in the propagation of flame in the limit mixtures is that represented by the equation:

$$CH_4 + O_2 = CO + H_2 + H_2O.$$

The general equation (1) was modified in accordance with this view, and the heat balances for all the limit mixtures calculated. It was found that Q, the heat evolved, and q, the heat unaccounted for or "lost," were practically proportional to one another, the heat unaccounted for averaging for each mixture 35 per cent. of the total evolved. The question of the variation with temperature of the heat transmitted from flames by conduction, convection, and radiation is discussed.

Attention is drawn to the preferential burning of hydrogen over carbon monoxide in the flame gases of all mixtures of which the ratio O_2/CH_4 was greater than 1·5.

253. "The propagation of flame in mixtures of methane and air. The uniform movement." By Richard Vernon Wheeler.

Mallard and Le Chatelier's determinations of the speed of travel of flame during the "uniform movement" in methane–air mixtures (*Ann. des Mines*, 1883, [viii], **4**, 324) were repeated.

It was shown that their results were incorrect, mainly because the methane they used, prepared from sodium acetate, was very impure.

The curve obtained on plotting speeds as ordinates, and percentages of methane as abscissæ showed that there was practically no difference between the speeds attained in mixtures containing from 9·4 to 10·5 per cent. of methane. On either side of these percentages the speeds diminished fairly regularly; but near the lower- and higher-limits of inflammability the curve flattened, more noticeably towards the higher-limit, becoming, ultimately, nearly horizontal.

The speed of travel of flame was found to be uniform throughout in the lower- and higher-limit mixtures, which contain (horizontal propagation of flame) 5·4 and 14·3 per cent. of methane respectively, and to be the same for both.

The following communications have been received during the vacation:

254. "The preparation of phenyl benzyl ether." By David Henry Peacock.

For the preparation of fairly large quantities of phenyl benzyl ether the ordinary method is neither convenient nor economical. According to Beilstein (3rd Ed., II, 1049), the compound is prepared by the action of benzyl chloride on potassium phenoxide. The method usually employed is to dissolve 94 grams (one molecule) of phenol in a concentrated solution of the equivalent quantity of potassium hydroxide, and then, after the addition of 128 grams (one molecule) of benzyl chloride and about 20 c.c. of alcohol, to heat on a water-bath under a reflux condenser for four hours. The yield of crude phenyl benzyl ether is only about 70 grams. A great disadvantage of this method is that the benzyl chloride and solution of potassium phenoxide do not mix, and therefore that reaction only occurs at their common surface. The liquid does not boil on the water-bath, which again militates against intimate contact.

It was found that the addition of copper powder as a catalyst greatly improved the yield; the following summary of two experiments shows this:

I. 9·4 Grams of phenol, 5·6 grams of potassium hydroxide in 5·6 c.c. of water, 2 c.c. of alcohol, and 12·8 grams of benzyl chloride heated on a water-bath for four hours—yield, 6·5 grams.

II. Same quantities as in I, but 0·1 gram of copper powder added—yield, 10·1 grams.

The final method of preparation adopted was the following:

Four hundred and seventy grams of phenol were dissolved in a solution of 280 grams of potassium hydroxide in 300 c.c. of water. This was heated to about 80°, and a mixture of 500 grams of benzyl chloride, 80 c.c. of alcohol, and 0·5 gram of copper powder added with frequent shaking. The mixture was heated under reflux in an oil-bath at 105—115°. It reacted vigorously at first, and was then kept in gentle ebullition for three hours. The non-aqueous layer was washed with warm water, dissolved in ether, and the solution dried. On removal of the ether and fractional distillation of the residue, 73 grams of benzyl chloride were recovered and 575 grams of phenyl benzyl ether obtained, a yield of about 90 per cent. of the theoretical, calculated from the benzyl chloride consumed.

Phenyl benzyl ether can be economically purified by fractional distillation under a pressure of 60—80 mm.

The method described above would obviously be applicable, after

suitable modification, in the preparation of ethers of substituted phenols, using other halogen derivatives than benzyl chloride.

255. "The capillary constants for liquid carbon monoxide and liquid argon. A correction." By C. A. Crommelin.

Whilst making calculations some time ago concerning the capillary constants of argon (Mathias, Onnes, and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 667, 960) errors were found in the tables of data given by Baly and Donnan in their paper on the surface-energies and densities of some liquefied gases (T., 1902, **81**, 907).

Below are given the corrected data for the surface-tensions of argon and carbon monoxide. Dr. G. Rudorf has already (*Ann. Physik*, 1909, [iv], **20**, 751) published the corrections for argon, but the complete tables for carbon monoxide and argon are conveniently given here.

TABLE XVIII (*corrected*).

Surface Tensions of Liquid Carbon Monoxide.

T	70	71	72	73	74	75	76	77
γ	12·11	11·88	11·64	11·41	11·18	10·96	10·73	10·50
T	78	79	80	81	82	83	84	85
γ	10·28	10·05	9·83	9·61	9·39	9·17	8·96	8·74
T	86	87	88	89	90			
γ	8·53	8·31	8·10	7·89	7·69			

TABLE XIX (*corrected*).

Surface Tensions of Liquid Argon.

T	84	85	86	87	88	89	90
γ	13·45	13·19	12·93	12·68	12·42	12·17	11·92

The γ-values for oxygen and nitrogen are correct.

256. "*p*-Chlorophenylselenious acid." (Preliminary note.) By Gilbert T. Morgan and J. Campbell Elliott.

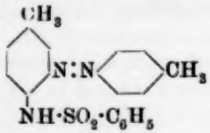
p-Chlorophenylselenocyanate, $C_6H_4Cl{\cdot}Se{\cdot}CN$ (yellow leaflets from alcohol, m. p. 50—51°), was obtained by adding an alcoholic solution of potassium selenocyanate to a well-cooled aqueous solution of *p*-chlorobenzenediazonium chloride containing excess of sodium acetate. The cyanide group was readily removed by the action of aqueous alkali hydroxide, and the resulting selenophenol, $C_6H_4Cl{\cdot}SeH$, oxidised to the diselenide, $(C_6H_4Cl{\cdot}Se)_2$, by hydrogen peroxide. Oxidation of either of these compounds with alkaline permanganate gave rise to sodium *p*-chlorophenylselenate.

p-Chlorophenylselenious acid, $C_6H_4Cl\cdot SeO_2H$ (colourless needles from hot water, m. p. 178°), was produced by boiling the preceding sodium salt with hydrochloric acid; it is an amphoteric substance, giving rise to metallic *p*-chlorophenylselenites and to salts of the mineral acids, such as the nitrate and hydrochloride. A more detailed examination of these aromatic selenium derivatives is in progress.

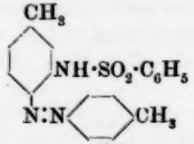
257. "Benzenesulphonyl derivatives of *o*-aminoazo-compounds." (Preliminary note.) By Gilbert T. Morgan and John Harbourne Cooke.

Benzenesulphonyl derivatives of aromatic *o*-diamines condense readily with aromatic nitroso-hydrocarbons in acetic acid solution, furnishing azo-derivatives.

4-Benzenesulphonyl-3:4-tolylenediamine and *p*-nitrosotoluene give rise to *4-benzenesulphonyl-4-amino-3-azotoluene* (I, golden-yellow needles, m. p. 151—152°). *3-Benzenesulphonyl-3-amino-4-azotoluene* (II, dark yellow needles, m. p. 156°), produced similarly from 3-benzenesulphonyl-3:4-tolylenediamine, is an acyl derivative of the still unknown 3-amino-4-azotoluene:



(I.)



(II.)

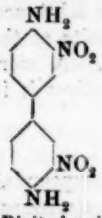
Experiments on the hydrolysis and oxidation of these azo-derivatives are in progress.

258. "The possibility of a new instance of optical activity without an asymmetric carbon atom." By Harold King.

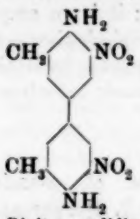
Up to the present time the only experimentally realised instances of optical activity in the absence of an asymmetric carbon atom are furnished by Perkin, Pope, and Wallach's (T., 1909, **95**, 1789) resolution of 1-methyl*cyclo*hexylideneacetic acid, and Mills and Bain's (T., 1910, **97**, 1866) resolution of the oxime, and later of other simple derivatives of *cyclo*hexanone-4-carboxylic acid. The molecular asymmetry of such substances belongs to the centro-asymmetric type.

The possibility of further examples of the centro-asymmetric type, differing widely from the previously known cases, is perceivable from the discovery by Cain and his co-workers of two *o*-dinitro-

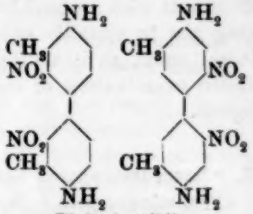
benzidines, two *o*- and four *m*-dinitro-*o*-tolidines of the formulæ shown below, each representing two isomerides:



o-Dinitrobenzidine.

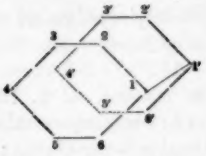


o-Dinitro-*o*-tolidine.



m-Dinitro-*o*-tolidines.

To explain the existence of these isomeric dinitrobenzidines and dinitrotolidines, Cain and Micklethwait (T., 1914, **105**, 1437) adopt Kaufler's spacial diphenyl formula as the basis:



On this assumption the two *o*-dinitrobenzidines, for example, are formulated, thus:

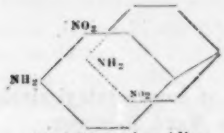
3 : 3'-Dinitrobenzidine.

3 : 5'-Dinitrobenzidine.

where the two planes of the benzene rings are superimposed, but not necessarily parallel to each other. The isomerism is ascribed to the non-rotation of one of the benzene rings. In the particular instance cited, Cain and Micklethwait have been unable to effect interconvertibility of the isomerides by any means, indicating the difficulty of free rotation of one of the rings relative to the other. A transformation, however, has possibly been effected in the case of the two *o*-dinitrotolidines. Now, Cain and Micklethwait find their difficulty in that they are quite unable to fix the orientation respectively of these pairs of isomerides; for example, in the case of the dinitrobenzidines they have no means of proving which is the 3 : 3'- and which the 3 : 5'-isomeride.

It occurred to the present author, however, that one of each of these pairs of isomerides presents a new instance of the centro-asymmetric type of enantiomorphous compound capable of resolu-

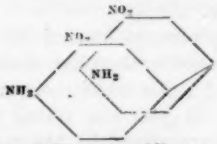
tion into its optically active isomerides. That such a possibility exists is evident from visual examination of the configurations of 3:5′-dinitrobenzidine and its mirror image:



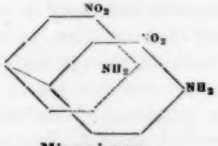
3:5′-Dinitrobenzidine.

Mirror image.

These configurations are unquestionably not identical in that they are not superimposable. 3:5′-Dinitrobenzidine should, therefore, be capable of resolution into its optically active isomerides. On the other hand, 3:3′-dinitrobenzidine is identical with its mirror image, as can be readily seen:



3:3′-Dinitrobenzidine.



Mirror image.

3:3′-Dinitrobenzidine is therefore unresolvable. It should be emphasised that these deductions are only valid if the underlying principle of Kaufler's spacial formula is accepted.

On the basis of the acceptation of Kaufler's formulæ for diphenyl and for other polycylic systems, the above considerations are capable of wide extension.

259. "Note on the dilution law."
By James Riddick Partington.

The empirical dilution law published by Kendall (T., 1912, **101**, 1275):

$$\frac{c\gamma^2}{1-\gamma} = K + k\frac{1-\gamma}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is identical with that proposed two years previously by the author on theoretical grounds (T., 1910, **97**, 1158), which may be written in the form:

$$\frac{c\gamma^2}{1-\gamma} = A + B\,.\,c\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A and B are constants.

The second term on the right of each equation is a correction

term, in the transformation of which it is legitimate to apply Ostwald's dilution law:

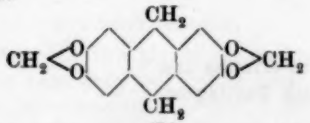
$$\frac{1-\gamma}{\gamma} = K'c\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thence, if $k = BK'$, equations (1) and (2) are identical.

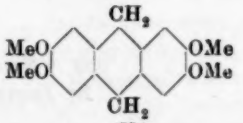
260. "A reaction of homopiperonyl and of homoveratryl alcohol." (Preliminary note.) By Gertrude Maud Robinson.

In 1909 Ewins (T., **95**, 1486) observed that homopiperonyl chloride readily underwent condensation under the influence of phosphorus pentachloride, yielding an almost insoluble substance, which he regarded as a dihydroanthracene derivative of the formula I. Owing, however, to the impossibility of oxidising it to an anthraquinone and to other experimental difficulties, it was not found possible definitely to prove this view.

Having had occasion to employ homopiperonyl alcohol in connexion with another investigation, the present author has observed its extreme sensitiveness to the action of acids which convert it into the substance described by Ewins. It was also found that homoveratryl alcohol, obtained with hydroveratroin by the reduction of veratraldehyde with sodium amalgam in aqueous-alcoholic solution, undergoes an analogous reaction, for example, on being warmed with a solution of sulphuric acid in glacial acetic acid. The product in this case is 2:3:6:7-*tetramethoxydihydroanthracene* (II), which is a more amenable substance than the piperonyl derivative, and was accordingly chosen for a more detailed investigation:



(I.)



(II.)

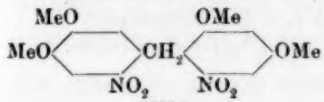
It is sparingly soluble in alcohol, and crystallises best from benzene in slender, colourless needles, melting at 227° and capable of distillation without decomposition. This substance is also obtained when veratrole is condensed with formaldehyde by means of 60 per cent. sulphuric acid, and this method was adopted for the preparation of the compound.

On demethylation with boiling hydriodic acid, followed by distillation of the product with zinc dust, 9:10-dihydroanthracene was obtained, whilst oxidation by heating with litharge yielded 2:3:6:7-*tetramethoxyanthracene*, a substance which crystallises from ethyl acetate in colourless prisms melting at about 135°, and

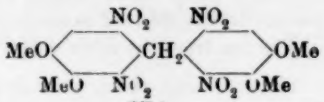
containing a molecule of solvent of crystallisation, or from alcohol in colourless needles melting at 173° and free from solvent. The dihydroanthracene is not fluorescent, whilst the corresponding anthracene derivative exhibits intense blue fluorescence in all its solutions.

On oxidation of 2:3:6:7-tetramethoxydihydroanthracene with 40 per cent. nitric acid, 4:5-dinitroveratrole and 6-nitroveratric acid were isolated, whilst more careful treatment with nitric acid in acetic acid or acetic anhydride solution resulted in the production of a substance, $C_{17}H_{18}O_8N_2$, which crystallises from acetic acid in pale yellow needles melting at 183°. This proves to be 6:6′-*dinitro*-3:4:3′:4′-*tetramethoxydiphenylmethane* (III), and its production involves the replacement of a methylene by two nitro-groups.

This derivative, on further boiling with nitric acid, yields a certain amount of dinitroveratrole and 2:2′:6:6′-*tetranitro*-3:3′:4:4′-*tetramethoxydiphenylmethane* (IV) as the main product. The latter substance crystallises from ethyl acetate in pale yellow, rhombic prisms, melting at 210°, and sparingly soluble in most organic solvents:



(III.)



(IV.)

Ewins (*loc. cit.*) treated dimethylenetetraoxydihydroanthracene with nitric acid, and obtained a product melting at 217°, for which he did not suggest a constitution. His analytical results agree excellently with the assumption that the substance is $C_{15}H_{10}O_8N_2$, and constituted analogously to the above-described dinitrotetramethoxydiphenylmethane.

261. "The preparation of 3-nitro-*o*-toluidine."

By John Henry Hadfield and James Kenner.

Considerable quantities of the above compound were required with a view to its conversion into 3-nitro-2-chlorobenzoic acid, the reactions of which it was desired to investigate. The preparation of the base according to the process described by Gnehm and Blumer (*Annalen*, 1898, **304**, 105) was, however, found to be inconvenient owing to the readiness with which decomposition set in. Systematic experiments, based on Wülfing's method for the preparation of *o*-nitroaniline (D.R.-P. 65212, 66060), were therefore instituted, and the following procedure was finally adopted.

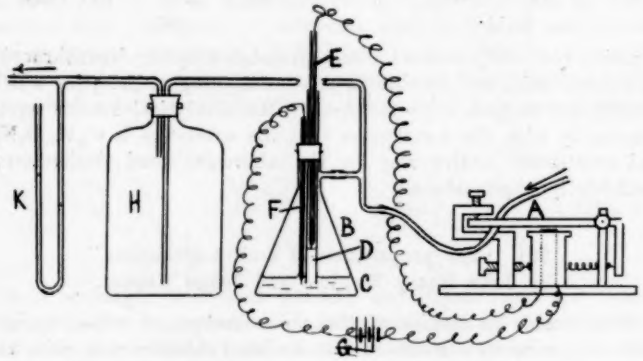
A mixture of oxalo-*o*-toluidide (18 grams) with concentrated

sulphuric acid (96 grams) was heated on the water-bath until a test portion was completely soluble in water. The product having been cooled to 50°, a mixture of nitric acid (D 1·42; 12 grams) with sulphuric acid (12 grams) was gradually added, the whole being well shaken and cooled to prevent any rise in temperature above 50°. After the pale red mixture had remained for some hours at the ordinary temperature, water (50 c.c.) was added, and the product was then heated in a reflux apparatus by means of an oil-bath at 140° until solution was complete. The temperature of the bath was then raised to 150°, and the heating continued for fifty minutes. The solution was then considerably diluted, and the base removed in a current of steam. In this manner 8·5 grams of base were obtained.

262. "Note on a gas-pressure regulator."
By Alfred Francis Joseph.

The regulator described was designed for use with a high and unsteady gas-pressure (about 20 cm. of water); it can be used to reduce to any desired pressure down to a few millimetres.

The gas from the main enters through a thin-walled rubber tube,



which passed between a fixed point and the hinged bar of an electro-magnet *A* (an old telegraph sounder was used). By means of a T-piece the tube is connected to a filter flask *B* containing 40 per cent. sulphuric acid *C*. *D* is a tube about 1 cm. in diameter fitting the stopper of *B* tightly, and *E* a narrow tube passing loosely into *D*, and provided with a platinum point and mercury contact; the height of the platinum point above the level of the

acid can be adjusted. *F* is another narrow tube with platinum point. *H* is a large bottle to take up small variations of pressure, and *K* a water manometer. The electro-magnet is put in series with *E*, *F*, and a battery *G*, so that when the gas-pressure forces the conducting acid up *D*, the circuit is closed, the electro-magnet excited, and the gas cut off. Any desired pressure is easily obtained by adjusting the height of *E*. The regulator appears to work equally well with low and high pressure in the gas main. The apparatus figured has been in use for more than a year; with an electromagnet having a resistance of about 100 ohms, a 6-volt battery is sufficient, and the current used is very small. A weight may be with advantage put on the hinged bar, oscillations in pressure being considerably reduced by its means. The regulator in use is arranged to keep the pressure at 5 cm., the amplitude of the oscillations being only in the neighbourhood of a millimetre.

Thursday, November 5th, 1914, at 8.30 p.m., Professor W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the following losses by death sustained by the Society during the vacation:

	Elected.	*Died.*
Joseph Bemrose	Dec. 4th, 1879.	May 26th, 1914.
Henry Boyers	Dec. 5th, 1901.	July 18th, 1914.
Jeffrey Hale Burland	Feb. 21st, 1884.	Oct. 9th, 1914.
Henry Fairrie	Feb. 21st, 1895.	Jan. 30th, 1914.
Harry Marshall Freear	May 7th, 1885.	Sept. 9th, 1914.
Edward Riley	Dec. 15th, 1851.	Sept. 12th, 1914.
Maung San U	Dec. 3rd, 1908.	July 17th, 1914.
William Frederick Keating Stock	June 21st, 1866.	June 22nd, 1913.
Robert Williamson	Dec. 4th, 1874.	Sept. 24th, 1914.

It was announced that a meeting of the Faraday Society will be held on Monday, November 23rd, at 8 p.m., when a general discussion on the "Hardening of Metals" will take place. Fellows of the Society are invited to attend the meeting.

Messrs. L. E. Hinkel and H. W. Cremer were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs:

Hugh Logie Allan, c/o The Burma Oil Co., Ltd., Rangoon, Burma.

Henry Atlas, 58 High Street, Dartford.

William Bacon, B.Sc., Springfield, Springfield Road, New Southgate.

Charles Kelway Bamber, The Martyrs, Crawley.

Srish Chandra Banerji, Department of Land Records and Agriculture, Cawnpore, U.P., India.

Durgasanker Bhattacharje, 3, Sitaram Ghose's Street, Calcutta, India.

Arthur Henry Bowell, University College, Auckland, New Zealand.

Alexander John Boyd, 64, Newbattle Terrace, Edinburgh.

John Bradshaw, M.Sc., Vernon House, Monument Park, Wigan.

Frank Brinsley, M.Sc.Tech., Berlin Villa, Stellenbosch, S. Africa.

James Mickle Brown, B.Sc., 176, Carter Knowle Road, Sheffield.

John Arthur Cresswick, Cress Dale, Villiers Street, Bexley, N.S.W., Australia.

Harry Cunliffe, 7, Rinkvale Cottages, Hawick.

James Ferguson, Langston, Harpenden, Herts.

Alexander Fleck, B.Sc., Hazelbank, Blenheim Avenue, Stepps, Glasgow.

George Noel Grinling, 62, Cartwright Gardens, W.C.

Charles Cochrane Iles, M.D., The Hampden Club, Phœnix Street, N.W.

George King, M.Sc., 25, Whitmore Road, Small Heath, Birmingham.

Herbert Levinstein, M.Sc., Ph.D., 24, Railway Approach, S.E.

Joseph Frederick Levy, 26, Compton Terrace, Highbury, N.

James Lyttle McKee, B.A., Ph.D., 4, Carrigside, Cork.

Alfred Edgar Newland, B.Sc., Government University, Pekin, China.

Henry Cecil Ratcliffe, 24A, Woodside Road, Bowes Park, N.

Joseph Drummond Robertson, The King's College, Taunton.

Rajkumar Sen, M.Sc., 14/3 Manicktola Street, Calcutta, India.

William Kershaw Slater, B.Sc., Eastdene, Chamber Road, Shaw, Oldham.

Henry Michael Spiers, B.A., B.Sc., Caius College, Cambridge.

Alan West Stewart, D.Sc., 29, Westbere Road, West Hampstead, N.W.

Mark Thompson, B.A., Queen's College, Cambridge.

Hugh Vivian, 25 Sketty Road, Swansea.

Of the following papers, those marked * were read:

***263. "The mechanism of the action of fused alkalis. Part I. The action of fused potassium hydroxide on dihydroxystearic acid and dihydroxybehenic acid." By Henry Rondel Le Sueur and John Charles Withers.**

The acid $C_{18}H_{34}O_5$ produced by the fusion of dihydroxystearic acid with potassium hydroxide (Le Sueur, T., 1901, **79**, 1313) is now shown to be α-hydroxy-α-octylsebacic acid:

$$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H \longrightarrow CO_2H\cdot C(OH)(C_8H_{17})\cdot[CH_2]_7\cdot CO_2H.$$

When α-hydroxy-α-octylsebacic acid is oxidised with potassium permanganate it gives θ-ketomargaric acid, $C_8H_{17}\cdot CO\cdot[CH_2]_7\cdot CO_2H$, and when it is heated above its melting point it gives a mixture of the two isomeric acids, $C_8H_{17}\cdot C(CO_2H){:}CH\cdot[CH_2]_6\cdot CO_2H$ and $C_7H_{15}\cdot CH{:}C(CO_2H)\cdot[CH_2]_7\cdot CO_2H$. These isomeric acids on reduction give α-octylsebacic acid, $CO_2H\cdot CH(C_8H_{17})\cdot[CH_2]_7\cdot CO_2H$.

Dihydroxybehenic acid on fusion with potassium hydroxide behaves like dihydroxystearic acid, and gives α-hydroxy-α-octyldodecanedicarboxylic acid:

$$C_8H_{17}\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_{11}\cdot CO_2H \longrightarrow CO_2H\cdot C(OH)(C_8H_{17})\cdot[CH_2]_{11}\cdot CO_2H.$$

The formation of α-hydroxy-α-octylsebacic acid and α-hydroxy-α-octyldodecanedicarboxylic acid from dihydroxystearic acid and dihydroxybehenic acid respectively involves the migration of the group C_8H_{17}· from one carbon atom to another adjacent to it, and it was pointed out that the migration of such a heavy group is very uncommon, if not hitherto unknown, in the aliphatic series.

***264. "Studies in the succinic acid series. Part II. Anilides and anilic acids and the effect of steric hindrance on the formation of the amides." By George Francis Morrell.**

Methods have been worked out to obviate the production of a large proportion of closed-chain products in the preparation of the open-chain neutral aniline derivatives of succinic acid and its methyl derivatives, and thus by improvements on the processes of Menschutkin (*Annalen*, 1872, **162**, 187) and of Tingle and Cram (*Amer. Chem. J.*, 1907, **37**, 597) succin- and methylsuccin-anilides have been obtained in excellent yield.

Of the acid aniline derivatives it was only necessary to investi-

gate methylsuccinanilic acid, which although theoretically existing in two isomeric forms:

$$\begin{matrix} CH_3\cdot CH\cdot CO_2H \\ | \\ CH_2\cdot CO\cdot NHPh \end{matrix} \quad \text{and} \quad \begin{matrix} CH_3\cdot CH\cdot CO\cdot NHPh \\ | \\ CH_2\cdot CO_2H \end{matrix},$$

was hitherto, in spite of all attempts to isolate the two substances by Anschütz, Auwers, Bone, and others, known only as a substance with a melting point given variously as 143°, 147°, and 149°. From methylsuccinic anhydride, and also methylsuccinanil, both of the isomerides have been prepared and isolated, the one melting at 159° and the other at 123°. They are particularly sensitive to heat in aqueous solution, being converted into gum-like substances, and this probably accounts for the more soluble of the two acids being previously overlooked.

The preparation of the neutral amides of the succinic acids can only be achieved from the esters by the action of ammonia, and it has been found that the most satisfactory results are obtained by allowing the methyl esters to react with aqueous ammonia in the cold, sufficient alcohol being added to procure solution. The use of alcoholic ammonia in a heated tube gives a much poorer yield (Fischer's method, *Ber.*, 1902, **35**, 844). Incidentally, cis- and trans-*dimethylsuccinamide* have been prepared for the first time; they melt and decompose at 244° and 238° respectively. The rate of amide-formation progressively falls off with the substitution of methyl groups in the succinic acid, and the results suggest that one is here dealing with a case of steric hindrance.

***265. "The alkaloids of quebracho bark. I. The constitution of aspidospermine." By Arthur James Ewins.**

Aspidospermine, $C_{22}H_{30}O_2N_2$, the most abundant alkaloid of *Aspidosperma Quebracho* (Quebracho blanco), has been found to contain one methoxyl group and an acetyl group which is attached to a nitrogen atom. It contains no *N*-methyl group.

When boiled with dilute mineral acids, aspidospermine loses its acetyl group, and a new crystalline base, *deacetylaspidospermine*, $C_{20}H_{28}ON_2$, is produced. This base on acetylation again yields aspidospermine. Deacetylaspidospermine (m. p. 110—111°) is an optically active diacidic secondary-tertiary base, which gives a crystalline *hydriodide*, $C_{20}H_{28}ON_2,2HI$ (m. p. 243°), a *monobenzoyl* derivative (m. p. 186—187°), and, on treatment with nitrous acid, a *nitro-nitroso*-derivative (m. p. 155—156°). With methyl iodide it gives a *compound*, $C_{20}H_{28}ON_2,2CH_3I$.

Aspidospermine, when boiled with concentrated hydriodic acid (D 1·7), gives a base, *aspidosine*, $C_{19}H_{26}ON_2$, derived from the

original alkaloid by simultaneous hydrolysis of the methoxyl group and removal of the acetyl group. It gives a crystalline *iodide*, $C_{19}H_{26}ON_2,HI$, melting at above 280°. Both this base and deacetylaspidospermine give intense colour reactions with ferric chloride and with oxidising agents generally.

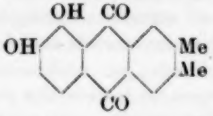
On oxidation with chromic acid, aspidospermine gives a crystalline *base* (m. p. 192—193°), which forms a sparingly soluble, crystalline *hydrochloride* (m. p. 286—287°). To this base the formula $C_{15}H_{24}O_2N_2$ is provisionally assigned.

266. "Some homologues of alizarin."
By Harry Bradbury and Charles Weizmann.

The authors have studied the condensations of hemipinic anhydride and 4-methoxyphthalic anhydride with *o*-xylene, and the following substances have been prepared:

Dihydroxy-2-xyloylbenzoic acid, isolated from the first condensation, crystallises from acetic acid in small needles melting at 238°. Its constitution is still a matter of doubt.

The above acid leads to the formation of two *dimethylalizarins*, but only the constitution of one of these has been definitely determined. This has been shown to possess the structure:



since it leads to the formation of pyromellitic acid by oxidation with potassium permanganate. This quinone melts at 276°, being more readily soluble in acetic acid than the other quinone melting at 198°, both of which crystallise in yellow needles, and resemble alizarin in properties.

The condensation of 4-methoxyphthalic anhydride with *o*-xylene is analogous in character to the above-mentioned, but in this case two *hydroxy-2-xyloylbenzoic acids* have been isolated. The acid obtained in greater quantity crystallises from acetic acid in small needles melting at 228°, and gives only one *hydroxydimethylanthraquinone*, which is of a pale green colour, and separates from acetic acid in needles melting at 210°.

The other acid was obtained only in small quantity, being more soluble in benzene than the former, and crystallises from this solvent in needles which melt at 184°.

267. "The reaction between benzylamine and the dibromosuccinic acids." By Edward Percy Frankland.

The action of benzylamine on *s*-dibromosuccinic acid (I) has been shown (T., 1911, **99**, 1775) to result in the formation of a dibenzylaminosuccinic acid and the dibenzylamide of *i*-tartaric acid:

$$\begin{array}{l} CO_2H\cdot CH\cdot Br \\ CO_2H\cdot CH\cdot Br \end{array} \qquad \begin{array}{l} CO_2H\cdot CH\cdot Br \\ Br\cdot CH\cdot CO_2H \end{array}$$

(I.) (II.)

The present investigations show that the isomeric acid (II) undergoes a similar reaction, yielding an isomeric dibenzylaminosuccinic acid (III), accompanied by a small quantity of the dibenzylamide of racemic acid (IV):

$$\begin{array}{l} CO_2H\cdot CH\cdot NH\cdot C_7H_7 \\ C_7H_7\cdot NH\cdot CH\cdot CO_2H \end{array} \qquad \begin{array}{l} C_7H_7\cdot NH\cdot CO\cdot CH\cdot OH \\ OH\cdot CH\cdot CO\cdot NH\cdot C_7H_7 \end{array}$$

(III.) (IV.)

From a comparison of the properties of the two dibenzylaminoacids it appears probable that the new acid has the racemic structure, analogous to II and to the more soluble diaminosuccinic acid which yields racemic acid with nitrous acid, whereas the previously described dibenzylaminosuccinic acid from *s*-dibromosuccinic acid has apparently a "meso" structure analogous to that of *s*-dibromosuccinic acid and the diaminosuccinic acid first obtained by Lehrfeld.

The action of benzylamine on *s*-dibromosuccinic acid has been reinvestigated with a view to isolate the products intermediate to the formation of dibenzylaminosuccinic acid, and thereby throwing light on the structural changes which would account for a symmetrical dibenzylamino-acid being derived from a symmetrical dibromosuccinic acid. So far the only intermediate products identified with certainty are benzylamine salts of bromomaleic acid. The isomeric acid (II) correspondingly yields salts of bromofumaric acid.

268. "The isomeric transformation of ammonium methyl sulphate and of substituted ammonium methyl sulphates. The interaction of amines and methyl sulphate" By Emil Alphonse Werner.

In a recent communication on the decomposition by heat of the methyl sulphates of certain *iso*carbamides evidence was obtained that ammonium methyl sulphate can undergo isomeric change in accordance with the equation:

$$NH_4MeSO_4 = NH_3Me\cdot HSO_4.$$

The reaction has been examined quantitatively, and a study of the change has been extended to a number of substituted ammonium

methyl sulphates, with the result that the property of undergoing isomeric transformation has been found to be common to all those derivatives where an interchange in the position of a hydrogen atom and a methyl group is possible, and may be represented by the general equations:

$$NH_3R\cdot MeSO_4 = NH_2RMe\cdot HSO_4.$$
$$NH_2RR'\cdot MeSO_4 = NHRR'Me\cdot HSO_4.$$
$$NHRR'R''\cdot MeSO_4 = NRR'R''Me\cdot HSO_4.$$

In the case of ammonium methyl sulphate and methylammonium methyl sulphate the change proceeded slowly up to 220°, above which it increased rapidly, and was almost complete at 275° after fifteen minutes' heating. With derivatives containing the phenyl group the isomeric change took place readily at much lower temperatures. Neither ammonium ethyl sulphate nor ammonium *n*-propyl sulphate undergoes any isomeric change.

The simple preparation of various substituted ammonium methyl sulphates from the interaction of amines and methyl sulphate takes place strictly in accordance with the equations:

$$NH_2R + Me_2SO_4 = NH_2RMe\cdot MeSO_4$$

and

$$NHR_2 + Me_2SO_4 = NHR_2Me\cdot MeSO_4,$$

and contrary to the conclusions arrived at by Ullmann (*Annalen*, 1903, **327**, 104), who obtained mixed products, which, it was pointed out, were no doubt the results of more or less isomeric change dependent on the rise of temperature allowed to take place during the interactions.

A theory of the mechanism of the isomerisation of the ammonium methyl sulphates based on dissociation as a preliminary to the change was suggested.

269. "Carboxylic acids derived from *cyclo*butane, *cyclo*pentane, *cyclo*hexane, and *cyclo*heptane." By Leonard James Goldsworthy and William Henry Perkin, jun.

The authors have prepared the *cis*- and *trans*-modifications of cyclo*butane*-1 : 2 : 3-*tricarboxylic acid*, and have devised an improved method of preparation of the *cis*- and *trans*-modifications of *cyclo*pentane-1 : 2 : 4-tricarboxylic acid. The *cis*- and *trans*-modifications of cyclo*hexane*-1 : 2 : 4-*tricarboxylic acid* and the *trans*-modification of cyclo*heptane*-1 : 2 : 4-*tricarboxylic acid* were also described.

270. "Resolution of *trans-cyclo*pentane-1 : 2-dicarboxylic acid." By Leonard James Goldsworthy and William Henry Perkin, jun.

The authors have succeeded in resolving *trans-cyclo*pentane-1 : 2-dicarboxylic acid by means of brucine. The d-*acid* melts at 181°,

and has α_D +87·6°; the d-*ethyl* ester boils at 170°/100 mm., and has α_D +70·31°, and the d-*anilide* melts at 245—247°, and has α_D +110·1°. The l-*acid* melts at 180—181°, and has α_D −85·9°; its *ethyl* ester boils at 170°/100 mm., and has α_D −69·76°.

271. "Investigations on the dependence of rotatory power on chemical constitution. Part X. The optical dispersive power of tetrahydro-2-naphthol and its esters." By Joseph Kenyon and Robert Howson Pickard.

The optical dispersive power of tetrahydro-2-naphthol is simple under conditions for which that of the 1-naphthylalkylcarbinols is complex. A convenient means of purifying *ac.*-tetrahydro-2-naphthol is by the crystallisation from water of the *sodium* salt of its hydrogen phthalate.

272. "A simple demonstration of the formation of biuret from the interaction of carbamide and cyanic acid." By Emil Alphonse Werner.

The current view, which is freely expressed in the text-books and works of reference, namely, that biuret is formed from the condensation of two molecular proportions of carbamide with los of one molecular proportion of ammonia, whilst true in substance, is quite fallacious as an explanation of the mechanism of the change.

It has been suggested by the author (T., 1913, **103**, 1014) that the production of biuret originates from the interaction of carbamide and its dissociation product, cyanic acid, in the "keto-form," HN:CO, a view which has the full support of experimental evidence, since it has been shown that the formation and decomposition of biuret is a truly reversible reaction (T., 1913, **103**, 2281).

A further proof in support of the truth of the above theory is supplied by the following simple experiment. To 3 grams of carbamide dissolved in 4 c.c. of concentrated hydrochloric acid diluted with 2 c.c. of water, 4 grams of powdered potassium cyanate are gradually added with constant stirring; after a short interval the solution (previously filtered to remove some cyamelide which has separated), when tested in the usual manner with copper sulphate and alkali, will be found to give a strong biuret reaction. Considering the very unfavourable conditions in the experiment, since the greater part of the cyanic acid is lost as the result of hydrolysis, polymerisation, and volatilisation, only a small proportion of biuret could be reasonably expected to be formed. An

estimation of the biuret produced in a rough experiment of this kind showed that approximately 4 per cent. of the theoretical amount, according to the equation:

$$NH{:}C(NH_2)\cdot OH + HNCO = NH[C(:NH)\cdot OH]_2$$ (*iso*-biuret or "enol-form"),

had actually been formed, and must have resulted as shown above, as no ammonia can have been removed from carbamide under the conditions of the experiment.

The formation of biuret in this way is of theoretical interest, since the reaction is strictly analogous to that by which substituted *iso*-biurets have been obtained by Bruce (*J. Amer. Chem. Soc.*, 1904, **26**, 449) from the isomeric transformation of certain *iso*carbamide cyanates.

273. "The corrosion of iron and its application to determine the relative strengths of acids." By John Albert Newton Friend and Charles William Marshall.

Iron readily corrodes when immersed in dilute solutions of the mineral salts of the alkali metals. The corrosion may, however, be inhibited by the addition of sodium carbonate. In general the amounts of carbonate required to produce inhibition bear a close relationship to the relative strengths of the acids of the mineral salts. The quantities of sodium carbonate required to inhibit corrosion in the presence of varying quantities of the same sodium salts have been determined. When the results are shown graphically a distinct resemblance can be traced to the specific conductivity curves of the free acids.

274. "Colorations produced by some organic nitro-compounds with special reference to tetranitromethane. Part I." By Ernest Magowan Harper and Alexander Killen Macbeth.

A fuller account of the work indicated in a preliminary note (P., 1913, **29**, 304) was given.

On mixing substances containing an unsaturated centre or an atom capable of exercising a higher valency with tetranitromethane the colour obtained deepens on keeping. Examination of the absorption spectra shows that they undergo a great change, a strongly selective effect developing with maximum of absorption at $1/\lambda$ 2850, approximately.

In the case of the mononitro-compounds the effect is absent save in the case of the alkyl nitrites. Deep colorations are obtained with all those examined when they are subjected to the same conditions

as tetranitromethane (see this vol., p. 15). An hypothesis was advanced to account for these colorations, and their analogy to those produced by tetranitromethane forms the basis of an hypothesis to account for the latter.

This postulates the isomerisation of one, or more, of the nitro-groups in tetranitromethane to a "nitritic" form. This also occurs in other polynitro-compounds containing more than two nitro-groups attached to the same carbon, or in substances containing two nitro-groups attached to the same carbon and a labile hydrogen atom.

275. "The absorption spectra of sulphurous acid and sulphites." By Robert Wright.

An examination of the absorption spectra of sulphurous acid and various sulphites and sulphonates points to the conclusion that aqueous sulphurous acid consists to a large extent of uncombined sulphur dioxide molecules. The absorption spectrum of gaseous sulphur dioxide strongly resembles that of the aqueous solution in that both exhibit the same band. The sulphites, on the other hand, show only general absorption.

276. "Rotatory power and refractivity. Part I. The rotatory powers, refractivities and molecular solution volumes of borneol, cinchonicine and benzoylcinchonicine in certain solvents." By David Henry Peacock.

Hitherto the explanations of the dependence of rotatory power on concentration have assumed a definite modification of the degree of asymmetry of the molecule. Livens (*Phil. Mag.*, 1913, [vi], **25**, 817) has shown that, assuming that the variation is solely due to variations in the velocity of light within the solution, $[\alpha]$ should vary as $(n^2-1)(n^2-1+1/a)$, where "a" is a constant and n = refractivity of the solution. For the solutions examined this appears to hold, and therefore the variations in $[\alpha]$ are not due to deformations of the molecule by the internal pressure of the solvent or other causes affecting the degree of asymmetry. Also for one solution it was shown that the variation in molecular solution-volume is probably to be ascribed to the variation in density of the solvent.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Carpenter, *Charles.* The purification of gas by heat. A Century's progress and its lessons. A Lecture delivered before the Institution of Gas Engineers at Liverpool, June 17th, 1914. London 1914. pp. 49. ill. (*Recd.* 27/10/14.) From the Author.

Coste, *John Henry,* and **Andrew** , *E. R.* The examination and thermal value of fuel: gaseous, liquid and solid. London 1914. pp. xvi + 278. ill. 6*s.* net. *Recd.* 27/10/14.) From the Authors.

Holland, *Frank William Crossley.* The pharmacy handbook. London 1914. pp. viii + 224. 6*s.* net. (*Recd.* 30/10/14.)

From the Publishers: Messrs. Henry Frowde, Hodder and Stoughton.

Institute of Chemistry of Great Britain and Ireland. History of the Institute 1877–1914. Compiled, . . . by *Richard B.* **Pilcher.** London 1914. pp. 307. ill. (*Reference.*) From the Council.

Lunge, *George.* Technical gas-analysis. London 1914. pp. xv + 407. 15*s.* net. (*Recd.* 5/11/14.) From the Author.

Lunge, *George* [*Editor*]. Technical methods of chemical analysis. English translation from the latest German edition, adapted to English conditions of manufacture, edited by *Charles Alexander* **Keane.** Vol. III., in two parts. London 1914. pp. xxxi + 1125. ill. £3 3*s.* net. (*Reference.*) From Dr. C. A. Keane.

Michaelis, *Leonor.* Die Wasserstoffionenkonzentration. Ihre Bedeutung für die Biologie und die Methoden ihrer Messung. Berlin 1914. ill. pp. xiv + 210. M.8.—. From the Author.

Purvis, *John Edward,* and **Hodgson,** *Thomas Reginald.* The chemical examination of water, sewage, foods, and other substances. Cambridge 1914. pp. vi + 228. 9*s.* net. (*Recd.* 31/10/14.) From the Authors.

Remington, *John Stewart.* Science and the miller. Liverpool 1914. pp. 166. (*Recd.* 3/9/14.) From the Author.

II. *By Purchase.*

Bühler, *F. A.* Filters and filter presses for the separation of liquids and solids. With additional matter relating to the theory of filtration and filtration in sugar factories and refineries by *John Joseph* **Eastick.** London 1914. pp. viii + 184. ill. 12*s.* net. (*Recd.* 21/10/14.)

Jellinek, *Karl.* Lehrbuch der physikalischen Chemie. Vol. I. Stuttgart 1914. pp. xxxvi + 732. M.24.—. (*Recd.* 19/6/14.)

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Tuesday, December 1st, 1914.

All persons who received grants in December, 1913, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Honorary Secretaries not later than Tuesday, December 1st.

The Council wish to draw attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

PAPERS TO BE READ AT ORDINARY SCIENTIFIC MEETINGS.

Fellows are reminded that a list of the papers to be read at each Ordinary Scientific Meeting will be advertised in the "Morning Post" on the Wednesday previous to the day of meeting, and will appear on the front page at the top of the extreme right-hand column.

At the next Ordinary Scientific Meeting on **Thursday**, November **19th**, 1914, at **8.30** p.m., the following papers will be communicated:

"The dissociation pressures of the alkali bicarbonates. Part II. Potassium, rubidium, and cæsium hydrogen carbonates." By R. M. Caven and H. J. S. Sand.

"Studies in the camphane series. Part XXXVI. *N*-Chloroaminocamphor." By M. O. Forster and M. Schlaepfer.

"Experiments on the removal of sulphur from silver." By C. C. Bissett.

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